TEXTILE RESEARCH JOURNAL

VOLUME XX November, 1950 *NUMBER 11*

PUBLICATION OF

TEXTILE RESEARCH INSTITUTE, INC.

Editorial Office: 10 East 40th Street, New York 16, N. Y.

Rayon Reports

Prepared Monthly by American Viscose Corporation, New York, N. Y. November, 1950

SPINNING ON CONES WINNING ACCEPTANCE

Mills Adopting New Idea to Reduce Shipping Costs

Decided interest in spinning on paper cones instead of wooden bobbins has been expressed by numerous woolen mills since the idea was first described in an article four months ago by the Avisco Textile Research Department. The first general demonstration of the system held at the Southern Textile Exhibition at Greenville, S. C. last month has also done much to popularize the new method.

The prime advantage of the new system is, of course, the savings it makes possible in shipping yarn. The chart below gives a quick comparison with bobbin shipping.

Comparative Shipping Weights of Yarn on Bobbins and Cones

BOBBINS		CONES	
Wt. of cardboard carton and straps	27½ lb.	Wt. of cardboard carton and straps	27½ lb.
Wt. of 96 wooden bobbins	61½ lb.	Wt. of 96 paper cones	20 lb.
Yarn weight	102 lb.	Yarn weight	96 lb.
Total shipping weight	191 lb.	Total shipping weight	143½ lb.
Yarn wt. to total shipping wt.	53.4%	Yarn wt. to total shipping wt.	66.9%

Another advantage with the cone system is the substantial reduction of the capital investment in wooden bobbins.

The procedure calls for a 11⅛" cone with a taper of 3°51'. This is placed on an inexpensive arbor with the rest of the spinning operation following as usual with the exception of a very slight adjustment in the pick-wheel. The present practice is to doff both arbor and full cone, replacing with an empty cone already on an arbor. Between doffs the spinner replaces the full cones with empty cones. A light tap with a metal rod inserted inside the tip of the cone drives out the arbor. By following this method, two sets of arbors per spinning machine should be the maximum needed under ordinary operations.

Spinning onto cones is being done at the Textile Research Dept., American Viscose Corporation. Demonstrations of the process can be arranged.

Avisco has available reprints of the article on this subject from August 1950 "Textile World." Copies are available on request.

RAYON 20 YEARS AGO

New York, November, 1930—Due to popular demand the Viscose Company is re-issuing its size chart which gives size figures for all articles of knit underwear.

New York, November, 1930—It is rumored that a method of manufacturing rayon from natural gas has been perfected.

Paris, November, 1930—Artificial furs made of rayon are an important fashion vogue at the present time.

MAKE USE OF *Avisco* 4-PLY SERVICE

To encourage continued improvement in rayon fabrics, American Viscose Corporation conducts research and offers technical service in these fields:

1 FIBER RESEARCH
2 FABRIC DESIGN
3 FABRIC PRODUCTION
4 FABRIC FINISHING

AMERICAN VISCOSE CORPORATION

America's largest producer of rayon

Sales Offices: 350 Fifth Avenue, New York 1, N. Y.; Charlotte, N. C.; Cleveland, Ohio; Philadelphia, Pa.; Providence, R. I.

TEXTILE RESEARCH JOURNAL

VOL. XX, No. 11 November, 1950

In This Issue

Mechanical Properties and the Structure of Hair
Cecil E. Reese and Henry Eyring 743

The Chemical Attack on Polymeric Materials as Modified by Diffusion
Sidney M. Katz, Edward T. Kubu, and James H. Wakelin 754

The Kinetics of Wool Dyeing: Part II: The Adsorption of Surface-Active Dyes by Wool and Other Fibers
P. Alexander and D. A. Charman 761

Letters to the Editor

The Relationship of Wax Content to Maturity of Cotton
A. N. J. Heyn 771

INDUSTRIAL SECTION

Use of Tabulator Data in the Analysis of Sliver and Roving Uniformity
John P. Elting and James C. Barnes 773

Conversion of the Saco-Lowell Sliver Tester to Electrical Recording
Ralph A. Rusca 780

"Orlon" Acrylic Fiber: Chemistry and Properties
R. C. Houtz 786

A Mechanized Fiber Blender
Lyle E. Hessler and Herbert E. Kieke 802

Trace Metals in Cotton Fiber
D. C. Heinzelman and R. T. O'Connor 805

Book Reviews 808

Editor: Julian S. Jacobs *Managing Editor:* Julia M. Crisp

Associate Editors

H. J. Ball
Earl E. Berkley
Henry Eyring
Gustavus J. Esselen
Earl K. Fischer
Milton Harris
K. L. Hertel
H. Mark
E. R. Schwarz
Kyle Ward, Jr.

TEXTILE RESEARCH JOURNAL, published monthly at Prince and Lemon Streets, Lancaster, Pa., is devoted to the interest of research in textile and allied industries. It is the official publication of Textile Research Institute, Inc.

Manuscripts and communications should be sent to the editorial offices, 10 East 40th Street, New York 16, N. Y.

Subscription rates (including, monthly, bound copy of the Abstracts from the *Journal of the Textile Institute*): General—$15.00 per year; additional for postage, 50 cents to Canada, $1.00 to all other countries. Special—$10.00 per year for United States and Canadian students, teachers, educational institutions, public libraries, governmental libraries and departments, plus 50 cents for postage to Canada. Single copies, $1.50 each.

Entered as second-class matter, April 27, 1945, at the postoffice at Lancaster, Pa., under the Act of August 24, 1912. Accepted for mailing at special rate of postage provided for in paragraph (d-2), Section 34.40, P. L. & R. of 1948, authorized May 9, 1950.

Contents copyrighted 1950 by Textile Research Institute, Inc.

Advertising rates supplied on request.

Do You Know

WHAT CAUSES BREAKDOWNS... REJECTIONS IN AUTOMATIC MACHINES?

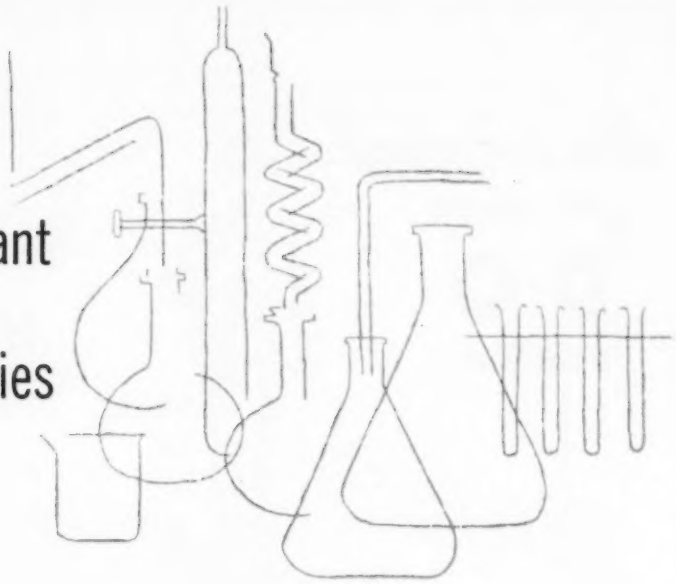
Fastax High-Speed Motion Picture Studies Have Been Made of:

- Machine Shop Tools Working.
- Failure of Rapidly Moving Mechanisms.
- Faulty Design Problems such as shattering relay contacts and cams.
- Gas and Liquid Flow . . . Combustion.
- High-Speed Weaving and Spinning Operations.
- Mechanical, Electrical, Physical and Anatomical Reflexes and Vibrations.
- Other applications too numerous to mention.

WRITE for catalog and information on how Wollensak can equip a high-speed laboratory for you . . . Completely portable and easy to use. Wollensak Optical Co., 813 Hudson Avenue, Rochester 21, N. Y.

Wollensak OPTICAL CO., ROCHESTER 21, N.Y.
MEANS FINE LENSES

check your textile chemical needs with Warwick's important series of chemical specialties for the textile industry



Warwick technical advisors, with their wide knowledge of textile chemicals and processes, are available for consultation.

- ANTILUSTROLE* dullers
- APPRAMINE* cationic softeners
- APPRETOLE* anionic softeners
- EUMERCIN* mercerizing assistants
- FORMASET* textile resins
- IMPREGNOLE* and NORANE* water repellents
- LANOLE* tar and grease removers
- ORGANOSOL coatings for textiles and paper
- PLASTISOL for coating and molding
- SETOLE* textile resins
- SULFANOLE* synthetic detergents
- WARCOFIX* color fixatives
- WARCO GFI* gas fading inhibitor
- WARCOLENE* finishing oils
- WARCONYL* fire retardants
- WARCOSAN* wetting and rewetting agents
- WARCOSOL* penetrants
- WEAVE-LOK* non-slip finish

WARWICK
CHEMICAL COMPANY

SUNTONE*
pigment printing colors for textiles and plastics

WARWICK CHEMICAL COMPANY, DIVISION Sun CHEMICAL CORPORATION 10th STREET and 44th AVENUE, LONG ISLAND CITY, NEW YORK

*REG. U. S. PAT. OFF.

Are you ready for those **D-O** *orders*

with Adequate Testing?

Priority rating **DO**-xx is certified under NPA Regulation 2. If you desire to extend this rating in accordance with NPA Regulation 2, extension must be made before_____19____

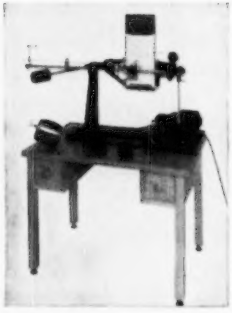
TESTED IS TRUSTED

Mr. Technician:

Let *Scott Testers simplify and codify your handling of orders. These machines safeguard purchasing, speed production, prove finished product is according to specification. They provide you with "picturized" charts which are easy to read and convenient to file as a guide to further production, as well as proof of quality. Especially valuable "for the record" in matters of renegotiation, contract termination, surplus disposal. Various models for tensile, burst, flexing, crepeage, twist, adhesion, from single fibre to 2,000 lbs.

*Registered Trademark

REQUEST CATALOG 50



IP-2

Patented Incline-plane Tester for tensile testing of yarn in single end in specimens as short as 1". Varying lengths other than standard can be tested, and the results obtained are comparable with tests of standard length. Capacities up to 4 lbs. tensile.

MODEL J

Model J provides for tensile testing of fabric; yarn in single end or skein; cord and twine. Also it may be equipped with Attachment W for ball burst test of knitted fabrics. Capacities up to 500 lbs. tensile.

SCOTT TESTERS, INC., 145 BLACKSTONE ST., PROVIDENCE 5, R. I.

Scott Testers — Standard of the World

TEXTILE RESEARCH JOURNAL

VOL. XX, NO. 11 November, 1950

Mechanical Properties and the Structure of Hair

Cecil E. Reese * and Henry Eyring

University of Utah, Salt Lake City, Utah

Abstract

A simple quantitative method for determining the amount of mechanical strength contributed by the various types of bonds in hair fiber has been developed. The effects of various types of reagents, such as acids, bases, oxidizing agents, and reducing agents, are discussed.

The reaction between various chemical agents and hair fibers has been found to be first-order with respect to the reagent and also with respect to the bonds to be broken. The effect of temperature is discussed. Using the theory of absolute reaction rates, the heats and entropies of activation for the reaction have been calculated.

The rate of diffusion into hair has been considered. Using Fick's second law of diffusion, the diffusion coefficient of hydroxyl ion in hair has been calculated. Also applying the theory of absolute reaction rates, the values for the heat and entropy of activation have been calculated.

THE MECHANICAL STRENGTH of fibrous materials is known to depend directly upon the number and type of primary and secondary bonds holding the individual fibers together. Many investigators in studying natural proteins such as hair [9, 12], wool [14], myosin [2], etc., have successfully characterized certain of the important types of bonds, and have discussed methods of removing the effects of these bonds. The discussion presented in this paper is the result of a successful attempt to quantitatively separate the mechanical-strength contributions of the different types of bonds, and to measure the rate of reaction between hair and various chemical reagents. The findings have been correlated with the proposed structural features common to most fibrous proteins.

The elastic and plastic deformation of hair depends markedly upon the number of secondary bonds—*i.e.*, salt-bridges; hydrogen bonds; and primary bonds, such as disulfide bonds between the polypeptide chains of the fiber. Any treatment which breaks any of these bonds alters the mechanical behavior of the fiber. The experimental data to be discussed were obtained using human hair, a natural keratin protein.

Each fiber was approximately 8 in. in length. By virtue of the technique employed, both ends, as well as the whole of the fiber, could be subjected to the same types of experiments and any change

* This work was carried out while Mr. Reese was a Fellow of the Textile Research Institute. Assistance from the Office of Naval Research is gratefully acknowledged.

due to ageing could be characterjzed. The effects of ageing on the accuracy of the measurements, which was within approximately 1%, were negligible. The cross-sectional areas were determined, neglecting the ellipticity of the fibers, from the diameters, which were determined with a microscope and a traveling eyepiece micrometer, the average of 10 measurements at different points in each fiber being used. The lengths of the fibers were measured with a cathetometer.

Before the fibers were subjected to the tests they were allowed to relax for a period of time ranging from 2 hrs. to 2 mos. at 100% relative humidity. After relaxation the fibers were dried in an atmosphere of 25%–40% relative humidity (measured using a sling psychrometer).

Stress-strain curves at constant rate of elongation and stress-time curves at constant elongation obtained for hair are typified by the curves in Figure 1. Elongation at constant rate is occurring from A to B; from B to J the curve is a stress-time curve, the fiber being under the different ambient conditions given in the legend on the figure. These curves were obtained using a modified Sookne-Rutherford [13] autographic balance constructed by Prof. Elton L. Quinn of the Chemistry Department, University of Utah, who has described the balance in another publication [11].

Figure 1 gives the response of a fiber under the conditions recorded in the legend. Before use, the hair was dried over $CaCl_2$ for a period long enough to remove all the water possible with this reagent. The region A–B shows the response of the fiber when dry and elongated at constant rate of elongation. The two general features common to all keratin protein fibers are easily observed. The extensions up to approximately 2% follow a Hooke's-law type of deformation. At about 2% extension plastic flow begins and continues at practically constant stress. From other experiments, the plastic flow continues up to 40% extension before any appreciable increase in stress is needed in order to maintain the rate of elongation constant. The shape of the curve during plastic deformation is only very slightly dependent upon the rate of elongation. At extensions much beyond 40% the fiber ruptures.

The remaining portion of the curve, B–J (Figure 1), is the stress-time curve. Dotted lines on the time axis and breaks in the curve indicate a lapse

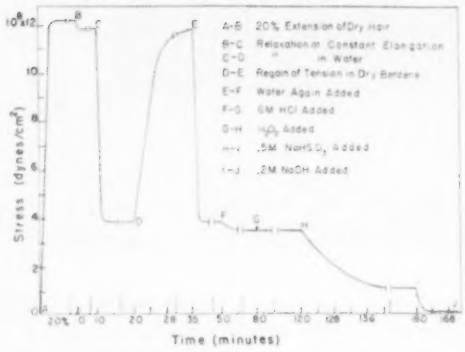

A–B 20% Extension of Dry Hair
B–C Relaxation at Constant Elongation in Water
C–D "
D–E Regain of Tension in Dry Benzene
E–F Water Again Added
F–G 6M HCl Added
G–H H_2O_2 Added
H–I .5M $NaHSO_3$ Added
I–J .2M NaOH Added
Stress (dynes/cm²)
Time (minutes)

FIG. 1. *The effect of various chemical agents on the tension in hair under elongation.*

of time during which the curve continues in a monotonic fashion.

The reaction of water with salt-bridges and hydrogen bonds is extremely rapid, as can be seen from segment C–D of Figure 1. The rate was too fast to measure accurately. Our experimental results indicate complete reaction in less than ½ sec. About 70% of the stress required to hold a fiber at 10% extension is due to the bonds that water breaks, the resultant change in stress being from 12×10^8 dynes/cm.² to 3.5×10^8 dynes/cm.². These bonds do not, however, determine the ultimate strength of the fiber.

In order to check whether water removed only the salt-bridges and the hydrogen bonds, or whether it also had some other effect, the water was removed with dry benzene. The fiber was then washed with benzene which had previously been dried over sodium, until no further change occurred in the stress-time curve. The curve D–E (Figure 1), indicates the re-formation of these bonds as water is removed. The response of the fiber to benzene had previously been checked by adding benzene to another dry, elongated fiber; no effect had been observed. This was rather surprising since according to the Astbury model [1] the nonpolar amino-acid side chains should attract each other more strongly in an atmosphere free from nonpolar solvent than they do in benzene. We therefore conclude that the polar groups attract so much more strongly than the nonpolar groups that the latter contribute little to the mechanical strength. It is interesting to note that upon drying wet hair the strength is nearly completely recovered. The

slow rate of recovery must be due to the slow, outward diffusion of the water and not to the slow re-formation of the bonds. However, a faster method of removing the water would be desirable in order to confirm this point.

Polar compounds other than water, such as the alcohols, cause the same release of tension, but at a slower rate. Thus, the polarity of the water apparently accounts for its effectiveness.

The curve E–F (Figure 1) illustrates the release of tension when water is added again. It is noted that the same equilibrium strength is reached in each case. The only reason for this step is to remove the polar bonds so that their larger contributions will not mask the effect of the other chemical reagents when they are added to the fiber.

One notices from segment F–G (Figure 1) that acids have only a small effect, a fact pointed out by others who have investigated animal hair. At room temperature (25°C), and concentrations as high as 6*M* HCl, the response of the hair, although fairly rapid, is relatively slight. Oxidizing acids, such as HNO_3, in concentrations ranging from 0.1*M* to 1*M* cause approximately the same response as is shown in F–G.

The curve G–H (Figure 1) shows the effect of H_2O_2 in slightly acid solution (pH < 6). The tension at a given elongation is not changed to a measurable degree by this reagent. What is true of this oxidizing agent is true for other oxidizing agents, such as 1*M* $KMnO_4$, KIO_3, $K_2Cr_2O_7$, etc. Black hair bleaches, but otherwise remains unaltered. There are at least three possible explanations for this: melanine does not contribute to the mechanical strength of the hair; or the configuration of the melanine which contributes to the mechanical strength is not responsible for the color; or the bonds which oxidize contribute the same amount before and after oxidation occurs. Of the three, the first seems to be the most logical. One thing which is apparent is that melanine is much more sensitive to oxidation than is the disulfide bond; in fact, from our experiments it appeared that the disulfide bond is rather resistant to oxidizing agents. This point is also confirmed by the remainder of the curve in Figure 1.

Phillips [5, 10], Harris [8], and others working with animal hair found evidence for the specificity of $NaHSO_3$ for part, if not all, of the disulfide linkages. From the curve H–I (Figure 1) the disulfide bonds, sensitive to this reagent, contribute to the mechanical strength at a fixed elongation. The rate of reaction is only moderately rapid. The percentage of the disulfide bonds which are removed by this reagent is discussed elsewhere in this paper. The actual decrease in tension in the work discussed here is from 3.5×10^8 dynes/cm.^{2} to approximately 1.5×10^8 dynes/cm.^{2} for the fiber held at a fixed length.

The final reagent added to the fiber was sodium hydroxide. The result is shown in the curve I–J (Figure 1). With this reagent the stress very rapidly approaches zero, but not until considerable time has elapsed does it actually reach zero stress. This is significant, since there are at least two types of linkages in the hair which are reactive to hydroxide ions: the more reactive disulfide bonds; and the bonds of the main polypeptide chains. The latter bonds hydrolyze in the presence of strong NaOH.

If sodium hydroxide and sodium bisulfite both react with the disulfide linkage, as has been supposed by other investigators [5, 8, 10], then sodium hydroxide must break a still greater percentage of these disulfide bonds. It is doubtful that the added effect is due to the hydrolysis of the polypeptide chains since the observed action is rapid, while hydrolysis of amide linkages is usually slow. Furthermore, there is an additional reaction which continues after the initial reaction is over, probably owing to hydrolysis of the polypeptide chains. Thus, we suppose that more of the disulfide bonds are sensitive to sodium hydroxide than to sodium bisulfite.

For a clearer picture of the process, consider the 3-element model used by Halsey, White, and Eyring [7] to predict many of the observed mechanical properties of fibers. Although the model needs modification in order to be useful in explaining all the mechanical properties of proteins, it will behave as a mechanical analog for the process which is graphed in Figure 1. (For a discussion of this model and various modifications see Burte, Halsey, and Dillon [4].)

The model consists of a spring in parallel with a spring in series with a dashpot, as shown in Figure 2. This model will behave in exactly the same way as the hair undergoing elongation graphed in Figure 1. When elongation ceases, the dashpot continues to relax until it no longer supports any stress. The whole stress then falls on the spring without a dashpot in series. We assume that each bond in cross section acts like a spring supporting

an equal load, on the average. The rate of decrease of the stress is then a measure of the rate of cutting of the bonds.

Most reactions between chemical reagents and hair are either too rapid or too slow to be measured by observing stress relaxation. As seen in Figure 1 the reagents NaOH and $NaHSO_3$ react at a rate which can easily be measured. In later investigations we found that Na_2S also reacted at a rate which was satisfactory for our method.

All of the experimental curves in this paper other than the portion A-C of Figure 1 show only the portion of the curve where the fiber is submerged in the specific reagent. The fibers were all elongated in water and allowed to come to equilibrium. Zero time was taken as the instant when the reagent was added.

Figure 3 is the stress-time curve for a hair at constant elongation when immersed in a solution of $NaHSO_3$ at room temperature. The curves for the various concentrations are shown in the figure.

The following kinetic considerations provided a satisfactory interpretation of the experimental facts. Assume the stress supported by the reactive bonds to be equal to the beginning maximum stress minus the final equilibrium stress. If we assume also that the tension is directly proportional to the number of bonds, then we may write

$$-\frac{db}{dt} = k'b(a + b), \tag{1}$$

where t = time, b = number of bonds, a = concentration of reagent after reaction, $a + b = C$ = initial concentration of the reagent, and k' = specific rate constant.

Integrating and evaluating the integration constants by applying the boundary conditions $t = 0$ and $b = b_0$ yields:

$$-\frac{1}{a}\ln\left(\frac{b}{b_0}\right) + \frac{1}{a}\ln\left(\frac{a + b}{a + b_0}\right) = k't. \tag{2}$$

Experimentally, we impose the condition $a \gg b$ by using only a single fiber of hair and a large volume of reagent of appreciable concentration surrounding the fiber. The expression thus reduces to

$$\ln\frac{b}{b_0} = -k'Ct. \tag{3}$$

The plot of $\ln\frac{b}{b_0}$ as a function of time is shown in Figure 4 for 0.1 M, 0.05 M, 0.01 M, 0.005 M, 0.001 M, and 0.0005 M $NaHSO_3$. The slopes of the curves for these plots are constant for the high concentrations, but when the concentration decreases the curves slope correspondingly less and less.

If we plot the slope $k'C_0$ as a function of concentration, the curve rises rapidly and reaches a maximum, where it remains over a large concentration range. This is a Langmuir-like type of adsorption isotherm, where chemical adsorption has occurred on reactive groups in the hair.

Consider the following reactions:

$$C + b \rightleftarrows Q,$$

where C = concentration of the reagents, b = number of bonds not forming a complex with C, and Q = number of "reagent-bond complexes."

The equilibrium constant is then

$$K = \frac{(Q)}{(C)(b)}. \tag{4}$$

Furthermore, since C and b must form a complex before reaction can occur, the rate of disappearance of the complex will also be the rate of disappearance of the number of bonds, or

$$\frac{db_t}{dt} = -k'Q, \tag{5}$$

where $b_t = b + Q$ is the total number of bonds. (6)

Substituting b from equation (4) into equation (6) yields:

$$b_t = Q\left[\frac{1}{KC} + 1\right]. \tag{7}$$

Solving for Q from equation (7) and substituting

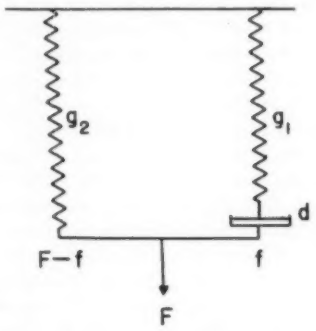


FIG. 2. *The 3-element model used to explain many of the mechanical properties of fibers.*

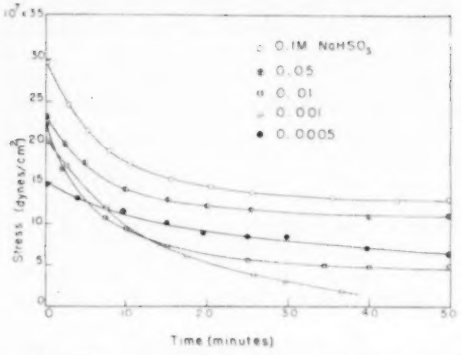


FIG. 3. *The rate at which sodium bisulfite affects the tension in hair fibers at constant elongation.*

into equation (5) yields:

$$\frac{db_t}{dt} = -\frac{k'KC}{1 + KC} b_t. \tag{8}$$

We have, after integration and evaluation of the integration constant, by setting $b_t = b_0$ at $t = 0$, the relation:

$$\ln \frac{b_t}{b_0} = -\left(\frac{k'KC}{KC + 1}\right) t. \tag{9}$$

Considering equation (9), if $1 \gg KC$, the value for the slope of the plot of $\ln \frac{b_0}{b_t}$ vs. t would be the same as $k'KC$, and, since $k'K$ is a constant, the rate of reaction would be directly proportional to the concentration. However, if $1 \ll KC$, then the concentration terms in equation (9) divide out and there would be no dependence of the rate of reaction on concentration. In Figure 5 the curve for $NaHSO_3$ illustrates both limiting cases.

We next determine the value of K as defined earlier. The measured slope of a plot of $\ln \frac{b_0}{b_t}$ vs. t is

$$\frac{k'KC}{1 + KC} = g. \tag{10}$$

Inverting and multiplying by k' gives

$$\frac{k'}{g} = \frac{1}{KC} + 1. \tag{11}$$

k' is the maximum value which g may reach as KC becomes large. Plotting $\frac{k'}{g}$ vs. $\frac{1}{C}$, the value of K is easily obtained. This gives $K = 2 \times 10^2$. The magnitude of this constant indicates that most of the reaction sites in the hair are covered by the reagent. The intercept of the plot is 1, as would be predicted by equation (11). (See Figure 6.)

Figure 7 shows the experimental stress-time curves obtained using sodium sulfide and sodium hydroxide at the concentrations given in the legend on the figure. The theoretical agreement is obtained by applying equation (3). Since the agreement is good, the kinetics of these reactions seem to follow a regular first-order reaction rate law.

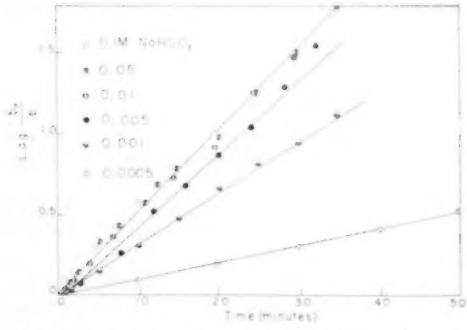


FIG. 4. *The rate of reaction between hair and sodium bisulfite at various concentrations, analyzed as a first-order reaction.*

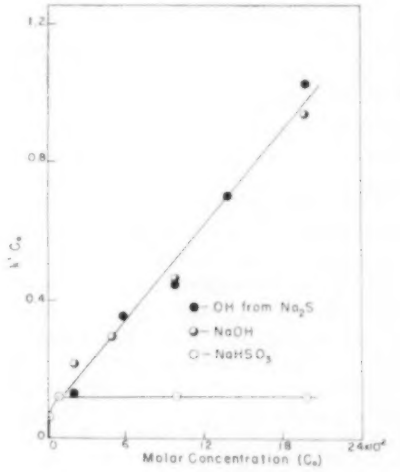


FIG. 5. *The effect of the concentration of the reagent on the rate of reaction.*

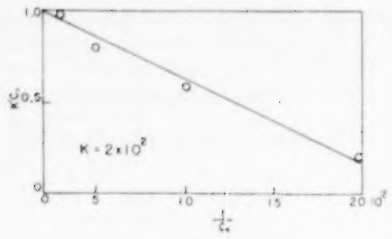


FIG. 6. *Langmuir-like analysis of the degree of adsorption of the reagent.*

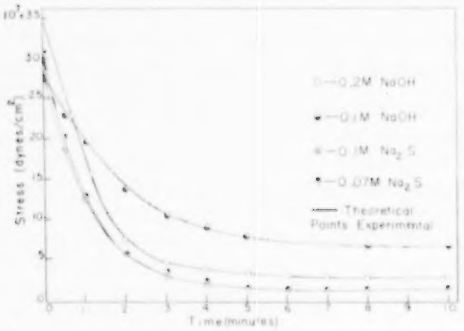


FIG. 7. *The time-dependent effect of fixed concentrations of sodium hydroxide and sodium sulfide on the tension in hair at fixed length.*

As the concentration of sodium hydroxide or sodium sulfide decreases, there is an unusual time lag before maximum rate of reaction is attained. (See the curves of Figures 8 and 9; concentrations are given in the legends.)

Using the kinetics given by equation (3), there is poor agreement between theoretical and experimental results at small values of the time. If we consider the mixing of the reagent and the bonds within the hair we see that the reagent must diffuse into the hair before reaction can occur. Since this diffusion will require time, it must be considered in the rate expression. Using Fick's second law, and adding a term which makes the concentration gradient time-dependent (since part of the diffusing reagent will react with the hair), we have in cylindrical coordinates:

$$\frac{\partial C}{\partial t} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 C}{\partial \theta^2} + \frac{\partial^2 C}{\partial Z^2}\right] - k'bC. \quad (12)$$

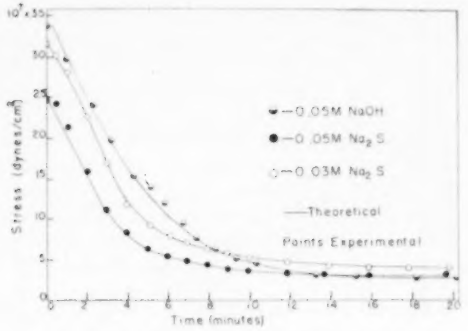


FIG. 8. *The effect of fixed concentrations of sodium hydroxide and sodium sulfide on the fiber tension at fixed length. An initial time lag in reaching maximum rate of reaction is shown. This is due to delay in the diffusion of the reagent into the fiber.*

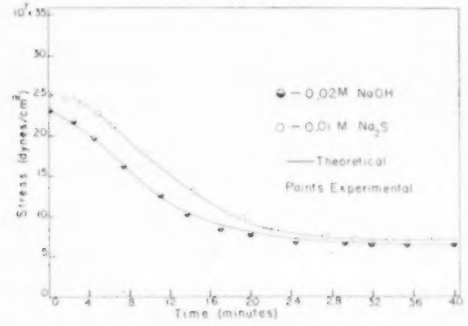


FIG. 9. *The effect of fixed concentrations of sodium hydroxide and sodium sulfide on the fiber tension at fixed length. An initial time lag in reaching maximum rate of reaction is shown. This is due to delay in the diffusion of the reagent into the fiber.*

Since in the fiber there is cylindrical symmetry, and thus no dependence upon θ, and because of the relatively long length of the fiber, there is no end effect and therefore no dependence upon Z. Equation (12) thus becomes

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial^2 C}{\partial r^2} + \frac{1}{r^2}\frac{\partial C}{\partial r}\right] - k'bC. \quad (13)$$

The term $k'bC$ arises from the reaction of the reagent with the bonds of the hair while diffusion is occurring. The solution considering $k'bC$ as a constant has been obtained, but, because of lack of enough known roots in Bessel's equation and

the mathematical cumbersomeness of the expression, only the solution neglecting $k'bC$ will be presented. The agreement between theoretical and experimental results using this approximation is good, as will be seen. The solution of equation (13) is [3]:

$$C = C_0 \left[1 - \frac{2}{a} \sum_{n=1}^{\infty} \frac{J_0(\lambda_n r)}{\lambda_n J_1(\lambda_n a)} e^{-\frac{D\lambda_n^2}{a^2} t} \right], \quad (14)$$

where C_0 = concentration of the reagent surrounding the fiber, D = diffusion coefficient, λ_n = the nth root of the zeroth-order Bessel function, a = radius of the hair fiber, and J_n = Bessel function of order n.

Equation (14) gives the concentration of the reagent at any position and at any time within the fiber. Let us assume that the rate of reaction in the fiber depends upon the average concentration only. The average concentration is:

$$\bar{C} = \frac{1}{\pi a^2} \int_0^a 2\pi C r dr. \quad (15)$$

Substituting the value of C from equation (14) into equation (15) yields:

$$\bar{C} = \frac{2}{a^2} \int_0^a C_0 \left[1 - \frac{2}{a} \sum_{n=1}^{\infty} \frac{J_0(\lambda_n r)}{\lambda_n J_1(\lambda_n a)} e^{-\frac{D\lambda_n^2}{a^2} t} \right] r dr. \quad (16)$$

Integrating, we obtain:

$$\bar{C} = C_0 \left[1 - \sum_{n=1}^{\infty} \frac{4}{\lambda_n^2} e^{-\frac{D\lambda_n^2}{a^2} t} \right]. \quad (17)$$

By substituting this expression for $\bar{C}$ into equation (3), we obtain for the rate of disappearance of the bonds in the hair:

$$-\frac{1}{b}\frac{db}{dt} = k'C_0 \left[1 - \sum_{n=1}^{\infty} \frac{4}{\lambda_n^2} e^{-\frac{D\lambda_n^2}{a^2} t} \right], \quad (18)$$

which integrates to:

$$-\ln b = k'C_0 \left[t + \sum_{n=1}^{\infty} \frac{4a^2}{\lambda_n^4 D} e^{-\frac{D\lambda_n^2}{a^2} t} + Q \right], \quad (19)$$

where Q is the integration constant.

From the values of the λ's (*i.e.*, $\lambda_1 = 2.405$, $\lambda_2 = 5.520$, $\lambda_3 = 8.654$, $\lambda_4 = 11.792$, etc.) we see that the roots of the Bessel function increase rapidly. Since D and a^2 are of about the same order of magnitude and since the roots are squared in the exponent, a good approximation is to neglect all the terms in the summation beyond the first.

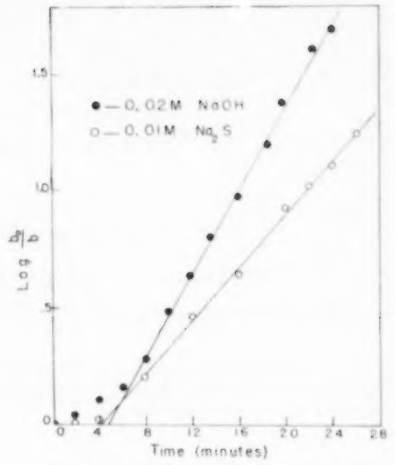


FIG. 10. *The rate of reaction between sodium hydroxide and hair and sodium sulfide and hair, analyzed according to first-order kinetics. (The time lag before maximum rate of reaction is shown.)*

By making this approximation and evaluating the integration constant, equation (19) becomes:

$$\ln \frac{b}{b_0} = -k'C_0 \left[t + \frac{4a^2}{D\lambda_1^4} \left(e^{-\frac{D\lambda_1^2}{a^2} t} - 1 \right) \right]. \quad (20)$$

This equation is unusable unless we can determine the value of $k'C_0$ and D. When the constant which multiplies t in the exponent is large, that term will rapidly approach zero. Thus, for large values for time the plot of $\ln \frac{b}{b_0}$ vs. t should be a straight line with a slope equal to $k'C_0$. The intercept of this line on the time axis should be equal to $\frac{4a^2k'C_0}{D\lambda_1^4}$, from which approximate values for D may easily be found. Such a plot is shown in Figure 10 for sodium hydroxide and sodium sulfide at the concentrations shown in the legend.

The values of $k'C_0$ and D are recorded in Table I for 3 reagents—sodium bisulfite, sodium hydroxide, and sodium sulfide. The values for $k'C_0$ were measured as described above. The values given for D are 10% higher than those found using the approximation discussed above. The more accurate values come from more laborious fitting to the experimental results. Since the agreement between theory and experiment for the reactions

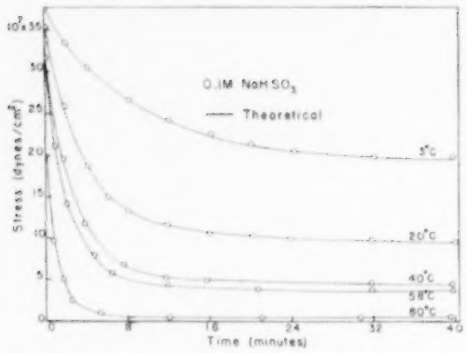


FIG. 11. *The effect of temperature on the rate of reaction between hair and sodium bisulfite. Also the ultimate amount of loss of strength by the hair.*

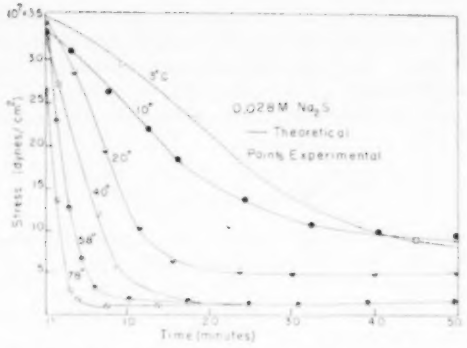


FIG. 12. *The effect of temperature on the rate of reaction between hair and sodium sulfide.*

between hair and sodium hydroxide and sodium sulfide was good, we decided to determine the order of the reaction with respect to the reagents. The plot of $k'C_0$ vs. C_0, as shown in Figure 5, yields a straight line with a slope of approximately 45°. Thus, the reaction is first-order with respect to the hydroxyl ion.

The straight line for sodium hydroxide (Figure 5) also explains the concentration dependence for sodium sulfide, assuming that the total effect is due to hydroxide ion formed by hydrolysis. The sulfide ion therefore appears to take only a small part in the reaction, and the hydrolysis is the important effect. In experiments similarly performed in a slightly acid medium (pH 6 and H_2S gas) there was some reaction, but it was so much slower than the reaction with hydroxyl ion that apparently the added effect of the sulfide ion reaction was unmeasurable in these experiments. For many reagents—$S^=$, CN^-, basic CH_3O, and others—it appears that the effect of the hydroxyl ion alone is important. The methods used here will distinguish between the rates in acid or basic media for these ions and will establish whether the reagent reacts with the hair or whether OH^- ion alone causes reaction.

TABLE I. CONCENTRATION DEPENDENCE OF THE RATE OF REACTION FOR THE REACTIONS BETWEEN VARIOUS REAGENTS AND HAIR AT 25°C

Reagent	Molar concentration	$k'C_0$ (min.$^{-1}$)	D (cm.^{2}/min.$\times 10^6$)
NaOH	0.2	0.90	*
NaOH	0.1	0.50	*
NaOH	0.05	0.30	1.50
NaOH	0.02	0.23	0.39
Na_2S	0.1	1.07	*
Na_2S	0.07	0.72	*
Na_2S	0.05	0.47	3.3
Na_2S	0.03	0.36	1.56
Na_2S	0.01	0.13	0.41
$NaHSO_3$	0.1	0.13	†
$NaHSO_3$	0.05	0.13	†
$NaHSO_3$	0.01	0.13	†
$NaHSO_3$	0.005	0.10	†
$NaHSO_3$	0.001	0.072	†
$NaHSO_3$	0.0005	0.028	†

* Reaction too fast to observe any diffusion.
† No time lag before maximum reaction rate.

One of the most useful methods at the disposal of the chemist in understanding chemical reactions is temperature studies. Using the theory of absolute reaction rates [6], one is able to compare certain of the thermodynamic quantities between the normal and the activated states and thus to better understand what happens to the reactants when reaction takes place. In order to obtain these quantities, a series of reactions were performed at different controlled temperatures for sodium bisulfite and sodium sulfide. These curves are shown in Figures 11 and 12. In these experiments the temperature was controlled within ±1°C over the desired temperature range. The fibers were elongated and allowed to "equilibrate" in water at the temperature at which the reactions were performed. When sodium bisulfite was used the concentration of reagent was high enough to insure that the reaction rate would be independent of the concentration (see Figure 5). Even if this assumption were

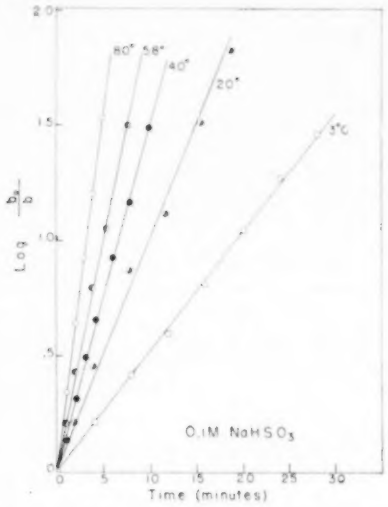


FIG. 13. *The variation of the rate constant with temperature for the reaction between hair and sodium bisulfite. Rates were calculated using a first-order equation.*

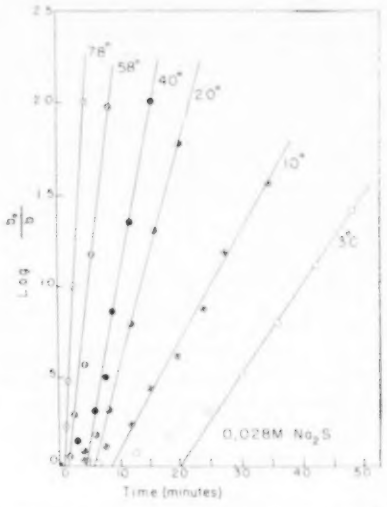


FIG. 14. *The variation with temperature of the rate constant for the reaction between hair and sodium sulfide. The reaction is first-order with respect to the bonds remaining to be broken.*

not valid, the value of the entropy of activation would change at most by 4 or 5 entropy units. This is not enough to change the general conclusions.

By plotting in Figures 13 and 14 the appropriate expression (equation (20)) for sodium bisulfite and for sodium sulfide (equation (20)), the values of the rate constants were determined; these are tabulated in Table II.

The values of ΔH^* and ΔS^* were determined by applying the general theory of reaction rates, using the familiar equation:

$$\ln \frac{k'}{T} = \ln \frac{k}{h} - \frac{\Delta H^*}{RT} + \frac{\Delta S^*}{R}. \qquad (21)$$

Thus, a plot of $\ln k'/T$ as a function of $1/T$ is a straight line with a slope of $\frac{\Delta H^*}{R}$ and an intercept of $\ln k/h + \frac{\Delta S^*}{R}$. Since k and h are well-known constants, the value of ΔS^* is known. The plots of equation (21) for sodium bisulfite and sodium sulfite are shown in Figure 15. The values of ΔH^* and ΔS^* are given in the legend.

The time lag before maximum rate of reaction is attained is present at all temperatures studied for sodium sulfide. Again considering this lag to be due to diffusion, the value of D at different temperatures was calculated. However, because of the large variation of the diffusion coefficients for small differences between the values of the intercept, this type of analysis is very difficult. More consistent results are obtained by using equation (18) in the following form:

$$\left(\frac{1}{b}\frac{db}{dt} + k'C_0\right) = k'C_0 \sum_{n=1}^{\infty} \frac{4}{\lambda_n^2} e^{-\frac{D\lambda_n^2}{a^2}t}. \qquad (22)$$

Now, considering only the first term of the summation because of the arguments used earlier, and

TABLE II. TEMPERATURE DEPENDENCE OF THE RATE OF REACTION FOR THE REACTIONS BETWEEN THE LISTED REAGENTS AND HAIR

0.1 *M* Sodium bisulfite			0.028 *M* Sodium sulfide		
Temp. (°C)	$1/T\times10^3$	$k'C_0$ (min.$^{-1}$)	Temp. (°C)	$1/T\times10^3$	$k'C_0$ (min.$^{-1}$)
3	3.64	0.119	3	3.64	0.113
20	3.41	0.220	10	3.55	0.153
40	3.19	0.343	20	3.41	0.269
60	3.00	0.510	90	3.19	0.380
82	2.82	0.710	58.1	3.03	0.774
			78	2.86	1.026

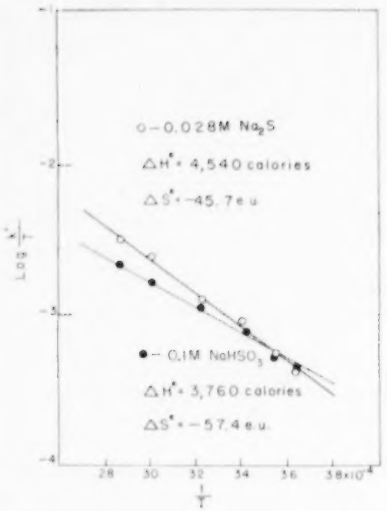


FIG. 15. *Rate of reaction as a function of temperature, showing the values of* $\Delta H^{\ddagger}$ *and* $\Delta S^{\ddagger}$ *for the reaction involved.*

taking the natural logarithm of both sides:

$$\ln\left(\frac{1}{b}\frac{db}{dt} + k'C_0\right) = \ln\frac{4k'C_0}{\lambda_1^2} - \frac{k'C_0D\lambda_1^2}{a^2}t. \quad (23)$$

The plot of $\ln\left(\frac{1}{b}\frac{db}{dt} + k'C_0\right)$ as a function of t yields a straight line for the various temperatures for sodium sulfide reagent, as shown in Figure 16. The slope of this line is equal to $\frac{k'C_0D\lambda_1^2}{a^2}$, and since all the terms except D are known the value of D is easily calculated. The value of D at various temperatures is tabulated in Table III. Also included are the values for the intercepts, both as calculated by equation (23) and as read from the plot (Figure 16). The value calculated from the intercept is smaller than that calculated from experimental results. This would be expected since equation (23) is only an approximation and equation (22) should be used for exact values.

Since the diffusion coefficient is equal to a specific rate constant multiplied by the distance between equilibrium positions squared—a result derived earlier (equation (13))—we may write:

$$D = \lambda^2 k'. \quad (24)$$

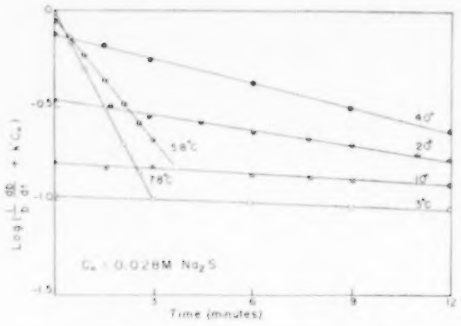


FIG. 16. *The diffusion coefficient for the hydroxyl ion diffusing in hair is obtained from these plots, as described in the text.*

By applying the same analysis to this rate as to any other:

$$\ln D = \ln\kappa\frac{kT}{h} - \frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} + \ln\lambda^2. \quad (25)$$

Thus, a plot of $\ln D/T$ as a function of $1/T$ would be a straight line with a slope equal to $\frac{\Delta H^{\ddagger}}{R}$. Such a plot is constructed in Figure 17. From this plot the value of $\Delta H^{\ddagger}$ for the process of diffusion is measured; this appears in Table IV. Also included are the values of $\Delta H^{\ddagger}$ for the reaction process. The value of $\Delta S^{\ddagger}$ for diffusion cannot be calculated unless some assumption is made for the value of λ, the equilibrium distance between molecular jumps. Assuming a value of 5Å., which appears to be about the correct value for the diffusion process, the value of $\Delta S^{\ddagger}$ is found to be equal to 10.5 e.u. The values of $\Delta S^{\ddagger}$ for reaction and for diffusion are also included in Table IV.

The magnitude of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the diffusion process is about twice that for ions diffusing in water, and about one-half that for nonelectrolytes

TABLE III. TEMPERATURE DEPENDENCE OF THE RATE OF DIFFUSION OF 0.028*M* SODIUM SULFIDE (OH^-) IN HAIR

Temp. (°C)	$1/T\times10^3$	D (cm.²/min.×10⁶)	Measured intercept	Theoretical intercept
3	3.64	0.080	0.108	0.078
10	3.55	0.093	0.133	0.106
20	3.41	0.17	0.230	0.187
40	3.19	0.55	0.333	0.263
58.2	3.02	2.31	0.680	0.516
98	2.85	3.97	1.000	0.712

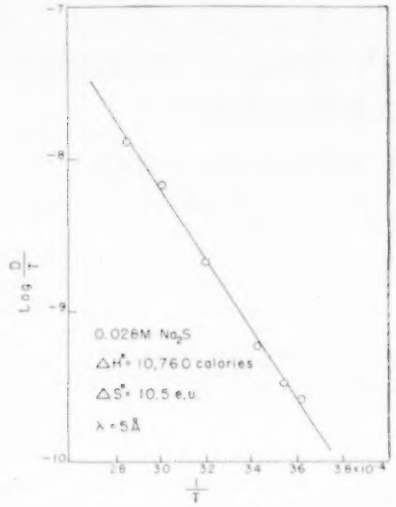


FIG. 17. *The variation of the diffusion coefficient as a function of temperature. The values of* $\Delta H^{\ddagger}$ *and* $\Delta S^{\ddagger}$ *are given for diffusion.*

diffusing in water. We therefore suggest that hair in the swollen state acts like a partially oriented membrane with water in many of the cavities in the fiber. The value $\Delta S^{\ddagger} = 10.5$ e.u. is of about the same order of magnitude as that for diffusion of ions through inorganic membranes. The value indicates some disorientation in the activated state, as compared to the normal state. This suggests that part of the bonds have been broken in going from the normal to the activated state.

The values of $\Delta H^{\ddagger}$ of 4,540 and 3,760 calories (heats of activation for the reaction processes) are unusually small. They are of about the same order of magnitude as that for conduction or for plastic flow, which indicates that the process is probably no more complicated than rotation of the ion until it is correctly oriented with respect to the reactive bond.

An alternative, but quite improbable, explanation would be that $\Delta S^{\ddagger}$ is near zero but that κ is much less than unity because the slow process involves leakage through an energy barrier. In this case the entropies $\Delta S^{\ddagger} = -45.7$ and -57.4 would only be apparent and would, instead, be measures of $\ln \kappa$. If these values measure $\Delta S^{\ddagger}$, then the great relative order of the activated state must involve very special orientation in the activated state or else many more normal than activated sites are open to the reagent.

TABLE IV. VALUES OF THE THERMODYNAMIC QUANTITIES FOR THE DIFFUSION RATES OF THE DIFFERENT REACTIONS (IN THE EQUATION $D = \lambda^2 k'$ FOR THE DIFFUSION COEFFICIENT, λ IS TAKEN TO BE 5 Å.)

Reactions	$\Delta H^{\ddagger}$ (cal.)	$\Delta S^{\ddagger}$ (e. u.)
Between $NaHSO_3$ and hair	4,540	−45.7
Between Na_2S and hair	3,760	−57.4
Diffusion of Na_2S into hair	10,760	10.5

Literature Cited

1. Astbury, W. T., *J. Chem. Soc.* **1942**, 337 (1942).
2. Astbury, W. T., and Sessions, W., *Proc. Roy. Soc. (London)* **A150**, 533 (1935).
3. Barrer, R. M., "Diffusion In and Through Solids," New York, Macmillan Company, 1941.
4. Burte, H., Halsey, G., and Dillon, J. H., TEXTILE RESEARCH JOURNAL **18**, 449 (1948).
5. Elsworth, F. F., and Phillips, H., *Biochem. J.* **35**, 135 (1941).
6. Glasstone, S., Laidler, K. J., and Eyring, H., "The Theory of Rate Processes," New York, McGraw-Hill Book Company, 1941.
7. Halsey, G., White, H. J., Jr., and Eyring, H., TEXTILE RESEARCH JOURNAL **15**, 295 (1945).
8. Harris, M., and Brown, A. F., *Am. Dyestuff Reptr.* **36**, 12 (1947).
9. Harrison, W., *Proc. Roy. Soc. (London)* **A94**, 460 (1918).
10. Phillips, H., and Lindley, H., *Biochem. J.* **41**, 34 (1947).
11. Quinn, E. L., A Description of a Modified Autographic Balance (in press).
12. Shorter, S. A., *Trans. Faraday Soc.* **20**, 228 (1924).
13. Sookne, A. M., and Rutherford, H. A., Jr., *J. Research Natl. Bur. Standards* **31**, 25 (1943).
14. Speakman, J. B., *Proc. Roy. Soc. (London)* **A103**, 377 (1928).

(*Manuscript received July 14, 1950.*)

The Chemical Attack on Polymeric Materials as Modified by Diffusion

Sidney M. Katz,* Edward T. Kubu,* and James H. Wakelin †

Contribution of the Textile Research Institute and Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

Abstract

The reaction of polymeric media with a chemical reagent generally involves the preliminary diffusion of the reagent through the polymer.

The effect of a relatively rapid diffusion of a chemical reagent into a cylindrical fiber on the overall rate of reaction is considered and the equation therefor is derived. The equation is applicable both to the extent of the reaction and to the decay of stress in the polymer, provided that a linear relationship between stress and extent of reaction is assumed.

Introduction

Although chemical reactions of swelling high polymeric substances are generally assumed to be homogeneous processes, the polymer and reagent form a heterogeneous two-phase system. Consequently, before a homogeneous reaction can occur it is necessary for the reactant to penetrate the swollen polymer phase by a diffusion process of finite duration.

In some instances, the progress of the reaction has been studied by chemical analysis of the polymer [20] or of the reagent attacking the polymer [1, 2]. Under these conditions, the kinetics of the process are directly determinable, and in the reaction of potassium permanganate with wool, for example, it has been claimed that the diffusion is the rate-controlling process [1, 2]. Menkart and Speakman [17] have reported that the reaction of mercuric acetate with wool is diffusion-controlled and have followed the reaction by observing the change in the resistance to extension.

In other cases, however, the chemical reaction of extended polymeric materials has been followed by the resultant stress relaxation [3, 15, 16, 18, 22–24]. Perhaps because many of these investigations were interpretable in terms of simple chemical kinetics, assuming a linear relationship between the tension and the extent of reaction, the effect of diffusion has been overlooked. To be sure, the process of diffusion by itself [4, 5, 19], the simultaneous diffusion and adsorption or reaction from a finite or infinite solution [9, 10, 14, 28], and the spherically symmetrical diffusion controlling a chemical reaction have been studied [6, 8]; but no investigation of the successive processes of diffusion and chemical reaction applicable to the study of textile materials appears to be available in the literature.

However, in the final stages of preparing this manuscript for press, a paper by Reese and Eyring [21] was brought to our attention. These authors have solved essentially the same problem that is considered here, but their method of solution and their basic assumptions differ from those employed in the present study. Because the divergence of our results and those reported by Reese and Eyring stems principally from the assumptions made in the course of the mathematical analysis, it was felt that it would be instructive to give some attention to a comparison of the two methods used in the analysis.

This paper presents the derivation of an equation expressing the extent to which a bimolecular chemical reaction within a textile fiber is modified by a diffusion process. From this equation the time rate of decay of tension, when the fiber is held at constant elongation, is related to the extent of chemical reaction. The basic assumptions involved in the evolution of this equation are discussed and

* Fellows of the Textile Research Institute, Princeton, New Jersey.

† Associate Director of Research, Textile Research Institute, Princeton, New Jersey.

two methods of solution are presented. The application of the resulting equation to experimental results is discussed.

Assumptions

The equation which will be presented herein is based upon an idealized model of the fiber-reagent system. We shall first consider the model and then discuss its relationship to experimental results.

It is assumed at first that the fiber is a uniform circular cylinder and, although uniformity is not an essential feature in stress-decay measurements, we consider that the stress is some function of the average cross section of the fiber. A circular fiber cross section is, however, essential to our derivation, and this condition is not completely realized in natural fibers. In many wool fibers and more predominantly in synthetic fibers, the assumption of a circular cross section appears to be a reasonable first-order approximation.

It is also assumed that the concentration of the reagent in the solution surrounding the fiber does not change during the reaction and that the concentration of reagent at the surface of the fiber is a function of the solution concentration and is therefore constant. That is, $c = c_0$ at $r = a$ for $t \geq 0$, where $c = c(r, t)$ is the concentration of the reagent in the fiber, r is the radial distance from the fiber center, a is the fiber radius, and t is the time.

We assume next that

$$\partial n / \partial t = -knc, \tag{1}$$

where $n = n(r,t)$ is the concentration of reactive groups in the fiber which remain to be attacked by the reagent. It may well be that some other kinetic equation is required for a particular system; in such case, the nature of the final equations will be altered, but the method of solving the equation will remain essentially the same.

In so far as the diffusion process is concerned, we shall assume as a first approximation that Fick's second law applies; that is,

$$\partial c / \partial t = D\nabla^2 c, \tag{2}$$

where D is the diffusion coefficient, considered to be independent of concentration. Crank points out [11] that a constant apparent diffusion coefficient gives a reasonably good approximation in the case of the absorption of dyes by textiles, although the true coefficient for the process may be a function of the concentration of dyestuff in the fiber.

The rigorous application of the last two assumptions leads to the following equation [14]:

$$\partial c / \partial t = D\nabla^2 c - knc. \tag{3}$$

This equation, however, in conjunction with equation (1), does not constitute a linear system and is difficult to solve. We shall assume, further, that the term $-knc$ may be neglected in comparison with the term $D\nabla^2 c$. This assumption is physically equivalent to the situation where diffusion is rapid but still of finite duration in comparison with the rate of the chemical reaction.

Finally, as a correlation between the extent of the chemical reaction and the tension, we postulate that, for constant fiber extension, the tension f at time t is proportional to the total number of unreacted groups present in an infinitesimally thin cross section of the fiber; that is,

$$f(t) = 2\pi M \int_0^a n(r,t) r dr, \tag{4}$$

where M is a proportionality constant. This relationship follows from an extension of the kinetic theory of rubber elasticity [12, 13, 25–27] to textile fibers, but it may be necessary to supplant it with some other form of correlation. In such a case, the final equations will be changed but the procedure will remain as outlined here.

The boundary conditions for the system have already been expressed: $c = c_0$ at $r = a$ for $t \geq 0$. In addition, the following initial conditions apply: $c = 0$ at $t = 0$ for $r < a$, and $n = n_0$ at $t = 0$ for $r \leq a$.

Mathematical Analysis

In terms of cylindrical coordinates, the solution of equation (2) with the above-mentioned conditions has been given [4, 7] as

$$c = c_0 - \frac{2c_0}{a} \sum_{l=1}^{\infty} e^{-Da_l^2 t} \frac{J_0(r\alpha_l)}{\alpha_l J_1(a\alpha_l)}, \tag{5}$$

where $J_0(r\alpha_l)$ is the zeroth-order Bessel function, $J_1(a\alpha_l)$ is the first-order Bessel function, and $a\alpha_l$ is the lth root of $J_0(a\alpha_l) = 0$.

Substitution of equation (5) into equation (1) yields

$$\left(\frac{\partial n}{\partial t}\right)_r = -kn\left[c_0 - \frac{2c_0}{a} \sum_{l=1}^{\infty} e^{-Da_l^2 t} \frac{J_0(r\alpha_l)}{\alpha_l J_1(a\alpha_l)}\right]. \tag{6}$$

Considered at constant r, the partial differential

becomes a total derivative which integrates to

$$\ln \frac{n}{n_0} = \frac{2kc_0}{aD} \sum_{i=1}^{\infty} (1 - e^{-D\alpha_i^2 t}) \frac{J_0(r\alpha_i)}{\alpha_i^2 J_1(a\alpha_i)} - kc_0 t, \quad (7)$$

and the over-all extent of reaction is given by integrating n over the cross section of the fiber. Therefore,

$$y = \frac{2\pi \int_0^a nr\, dr}{\pi a^2 n_0}$$

or

$$y = \frac{2}{a^2} e^{-kc_0 t} \int_0^a \exp\left\{ \frac{2kc_0}{aD} \sum_{i=1}^{\infty} (1 - e^{-D\alpha_i^2 t}) \times \frac{J_0(r\alpha_i)}{\alpha_i^2 J_1(a\alpha_i)} \right\} r dr, \quad (8)$$

where y is the fraction of bonds unreacted at time t.

Because of the nature of equation (4), the relative tension of the fiber, f/f_0, where f_0 is the tension at $t = 0$, is identically equal to the extent of reaction, y. The symbol Z will be used in the subsequent equations to signify both the extent of reaction, y, and the relative tension, f/f_0.

By defining the dimensionless quantities $\beta_i = a\alpha_i$, $\rho = r/a$, $T = Dt/a^2$, and $\delta = \frac{2kc_0 a^2}{D}$, and taking logarithms, equation (8) becomes

$$\ln Z = -\frac{\delta}{2} T + \ln 2 \int_0^1 \exp\left\{ \delta \sum_{i=1}^{\infty} (1 - e^{-\beta_i^2 T}) \times \frac{J_0(\rho\beta_i)}{\beta_i^2 J_1(\beta_i)} \right\} \rho d\rho, \quad (9)$$

or

$$\ln Z = -kc_0 t + A = -\frac{\delta}{2} T + A, \quad (10)$$

where

$$A = \ln 2G$$

and

$$G = \int_0^1 \exp\left\{ \delta \sum_{i=1}^{\infty} (1 - e^{-\beta_i^2 T}) \frac{J_0(\rho\beta_i)}{\beta_i^2 J_1(\beta_i)} \right\} \rho d\rho.$$

We let

$$E_i = \frac{(1 - e^{-\beta_i^2 T})}{\beta_i^2 J_1(\beta_i)},$$

and expand the argument of the exponential, so that

$$G = \int_0^1 \rho d\rho + \int_0^1 \delta \sum_{i=1}^{\infty} E_i J_0(\rho\beta_i) \rho d\rho + \frac{1}{2!} \int_0^1 \delta^2 \left\{ \sum_{i=1}^{\infty} E_i J_0(\rho\beta_i) \right\}^2 \rho d\rho + \frac{1}{3!} \int_0^1 \delta^3 \left\{ \sum_{i=1}^{\infty} E_i J_0(\rho\beta_i) \right\}^3 \rho d\rho + \ldots \quad (11)$$

For values of δ less than 10 this series converges satisfactorily. The first three terms integrate directly, if it is borne in mind that each of the cross products in the quadratic term, such as

$$\int_0^1 \delta^2 \sum_{i,j}^{\infty}{}' E_i J_0(\rho\beta_i) E_j J_0(\rho\beta_j) \rho d\rho, \; i \neq j,$$

vanishes identically because of the orthogonality of the Bessel functions with respect to ρ. In expanding the cubic term of equation (11), products of the following form are encountered:

$$\int_0^1 \delta^3 \sum_{i=1}^{\infty} E_i^3 J_0^3(\rho\beta_i) \rho d\rho,$$

$$\int_0^1 \delta^3 \sum_{i,j}^{\infty}{}' E_i^2 J_0^2(\rho\beta_i) E_j J_0(\rho\beta_j) \rho d\rho, \; i \neq j,$$

and

$$\int_0^1 \delta^3 \sum_{i,j,k}^{\infty}{}' E_i J_0(\rho\beta_i) E_j J_0(\rho\beta_j) E_k J_0(\rho\beta_k) \rho d\rho, \quad i \neq j \neq k.$$

Of these, the first provides the largest contribution, but this is appreciable only for small integral numbers of the running parameter l. Accordingly, the first term has been integrated and we obtain

$$\int_0^1 \delta^3 \sum_{i=1}^{\infty} E_i^3 J_0^3(\rho\beta_i) \rho d\rho = \frac{\delta^3}{12} \sum_{i=1}^{\infty} (1 - e^{-\beta_i^2 T})^3 \frac{1}{\beta_i^6} - \frac{3}{1024} \delta^3 \sum_{i=1}^{\infty} (1 - e^{-\beta_i^2 T})^3 \frac{1}{\beta_i^4} - \frac{3}{512} \delta^3 \int_0^1 \sum_{i=1}^{\infty} (1 - e^{-\beta_i^2 T})^3 \frac{\rho^2}{\beta_i^2} \frac{J_0^2(\rho\beta_i)}{J_1^2(\beta_i)} d\rho + \frac{21}{1024} \delta^3 \int_0^1 \sum_{i=1}^{\infty} (1 - e^{-\beta_i^2 T})^3 \frac{\rho^2}{\beta_i^2} \times \frac{J_1^2(\rho\beta_i) J_0(\rho\beta_i)}{J_1^2(\beta_i)} d\rho. \quad (12)$$

Taking only the first term of equation (12), G may be expressed thus:

$$G = \frac{1}{2} + \delta \sum_{i=1}^{\infty} (1 - e^{-\beta_i^2 T}) \frac{1}{\beta_i^4} + \frac{\delta^2}{4} \sum_{i=1}^{\infty} (1 - e^{-\beta_i^2 T})^2 \frac{1}{\beta_i^6} + \frac{\delta^3}{12} \sum_{i=1}^{\infty} (1 - e^{-\beta_i^2 T})^3 \frac{1}{\beta_i^8}. \quad (13)$$

TABLE I

$$B = \sum_{i=1}^{\infty} (1 - e^{-\beta_i^2 T}) \frac{J_0(\rho\beta_i)}{\beta_i^2 J_1(\beta_i)}$$

Values of B for the following values of ρ

T	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0.01	0.00500	0.00500	0.00500	0.00500	0.00500	0.00500	0.00499	0.00495	0.00470	0.00353	0
0.02	0.01000	0.01000	0.01000	0.01000	0.01000	0.00997	0.00984	0.00945	0.00833	0.00558	0
0.05	0.02494	0.02493	0.02487	0.02472	0.02438	0.02366	0.02232	0.01992	0.01589	0.00950	0
0.1	0.04813	0.04795	0.04734	0.04636	0.04329	0.04157	0.03748	0.03176	0.02392	0.01348	0
0.5	0.11730	0.11616	0.11275	0.10704	0.09900	0.08859	0.07582	0.05873	0.04296	0.02276	0
1.0	0.12456	0.12332	0.11959	0.11338	0.10468	0.09345	0.07976	0.06169	0.04490	0.02353	0
2.0	0.12498	0.12374	0.11999	0.11375	0.10501	0.09374	0.07999	0.06186	0.04502	0.02376	0

Since

$$\ln Z = -\frac{\delta T}{2} + \ln 2G,$$

$$\ln Z = -\frac{\delta T}{2} + \ln\left\{1 + 2\delta \sum_{i=1}^{\infty} (1 - e^{-\beta_i^2 T}) \frac{1}{\beta_i^2} + \frac{\delta^2}{2!} \sum_{i=1}^{\infty} (1 - e^{-\beta_i^2 T})^2 \frac{1}{\beta_i^4} + \frac{\delta^3}{3!} \sum_{i=1}^{\infty} (1 - e^{-\beta_i^2 T})^3 \frac{1}{\beta_i^6}\right\}. \quad (14)$$

It is instructive to compare equation (14) for the extent of reaction, Z, with that obtained by Reese and Eyring [21], who have considered the solution of the same diffusion equation. They have made the assumption that the rate of reaction depends upon the average concentration of the reactant throughout the fiber and not on the concentration at a given distance along the radius of the fiber as predicted by the solution of Fick's equation. For the purposes of this comparison we may write their final result for the extent of reaction using our notation (equation (19), page 749):

$$\ln Z = -\frac{\delta T}{2} + 2\delta \sum_{i=1}^{\infty} (1 - e^{-\beta_i^2 T}) \frac{1}{\beta_i^4}. \quad (15)$$

Equation (14) will reduce to equation (15) if we consider only the first two terms of the logarithmic argument of the former and, further, if it is recalled that

$$x = \ln(1 + x) \text{ for } x << 1,$$

where

$$x \equiv 2\delta \sum_{i=1}^{\infty} (1 - e^{-\beta_i^2 T}) \frac{1}{\beta_i^4}.$$

The assumption that the average concentration is effective in governing the rate of reaction holds only for small values of the argument $\delta (= (2kc_0a^2)/D)$. For values of δ appreciably larger than unity, the diffusion coefficients predicted by equation (15) will be less than their true values by the amount that the value of A evaluated on this basis departs from the value found by taking the more complete integral (equation (14)). This, no doubt, may account for a substantial part of the 10% to 20% discrepancy between calculated and observed diffusion coefficients reported by Reese and Eyring. It is also important to note that the extent of reaction predicted by equation (14) is essentially a power series in the reciprocal of the diffusion coefficient and therefore cannot be related to the simple inverse of D except for small values of $(kc_0a^2)/D$, as has already been mentioned.

Finally, the solution of equation (9) was carried out numerically, employing Simpson's one-third rule, as a check on the accuracy of equation (14) and the range of δ values covered by it. Table I lists

TABLE II

CALCULATION OF $A = \ln 2\int_0^1 e^{\delta B}\rho d\rho$

($\delta = 1.0$ and $T = 0.5$)

ρ	B	δB	$e^{\delta B}$	$\rho e^{\delta B}$	x_m	$x_m\rho e^{\delta B}$
0	0.11730	0.11730	1.1244	0	1	0
0.1	0.11616	0.11616	1.1232	0.1123	4	0.4492
0.2	0.11275	0.11275	1.1193	0.2239	2	0.4478
0.3	0.10704	0.10704	1.1129	0.3339	4	1.3356
0.4	0.09900	0.09900	1.1041	0.4416	2	0.8832
0.5	0.08859	0.08859	1.0926	0.5463	4	2.1852
0.6	0.07582	0.07582	1.0787	0.6472	2	1.2944
0.7	0.05873	0.05873	1.0604	0.7423	4	2.9692
0.8	0.04296	0.04296	1.0439	0.8351	2	1.6702
0.9	0.02276	0.02276	1.0231	0.9208	4	3.6832
1.0	0	0	1.0000	1.0000	1	1.0000
						15.9180

$$\int_0^1 e^{\delta B}\rho d\rho = \frac{0.1}{3} 15.9180 = 0.5306$$

$$A = \ln 1.0612 = 0.0594$$

values for B given by

$$B = \sum_{i=1}^{\infty} (1 - e^{-\beta_i^2 T}) \frac{J_0(\rho\beta_i)}{\beta_i^2 J_1(\beta_i)},$$

necessary for the calculation of A, where

$$A = \ln 2 \int_0^1 \exp\{\delta B\} \rho d\rho,$$

at specified values of T and ρ. Since the series for B converges relatively slowly, the numerical calculation requires the summation of fifteen terms of the series in order to insure an accuracy for B to at least four significant figures. Table II gives a sample calculation for equation (9) for $\delta = 1.0$ and $T = 0.5$.

Application to Experimental Results

The effect of diffusion on a bimolecular reaction as considered in this paper is indicated in Figure 1. Here curves are shown for values of $\delta = 1.0$, 3.0, 7.0, and 10.0 (curves B, C, D, and E, respectively) calculated from equation (14) which illustrate the effect of diffusion if kc_0a^2 is considered constant. Curve A represents the curve expected from first-order kinetics when no diffusion effect is operative. It should be noted that for relatively large values of δ the curve does not approach the limiting slope, -1, within the region plotted, and, from the experimental standpoint, large values of time have to be taken into account in order to evaluate the diffusion effect properly. Conceivably, for certain combinations of kc_0, a^2, and D, the reaction may be diffusion-controlled throughout the measurable region of the experimental parameter used in the determination of Z.

The method of evaluation of experimental data is indicated in Figure 2, in which the curve for $\delta = 1$ is reproduced from Figure 1. The term kc_0 may be evaluated from the slope of the linear part of the curve when $\ln Z$ is plotted against t in the region where diffusion is no longer controlling the reaction. The vertical displacement of the linear part of the curve (Figure 2) for a diffusion-controlled reaction above that for a reaction with no diffusion effect is designated as A_∞, which may be directly related to the diffusion coefficient if the radius of the fiber is known, since

$$A_\infty = \ln 2G_\infty \text{ at } t = \infty$$

and

$$G_\infty = \frac{1}{2} + \delta \sum_{i=1}^{\infty} \frac{1}{\beta_i^4} + \frac{\delta^2}{4} \sum_{i=1}^{\infty} \frac{1}{\beta_i^6} + \frac{\delta^3}{12} \sum_{i=1}^{\infty} \frac{1}{\beta_i^8}, \quad (16)$$

or

$$G_\infty = \frac{1}{2} + 3.1252 \times 10^{-2}\delta + 1.302 \times 10^{-4}\delta^2 + 7.4 \times 10^{-5}\delta^3.$$

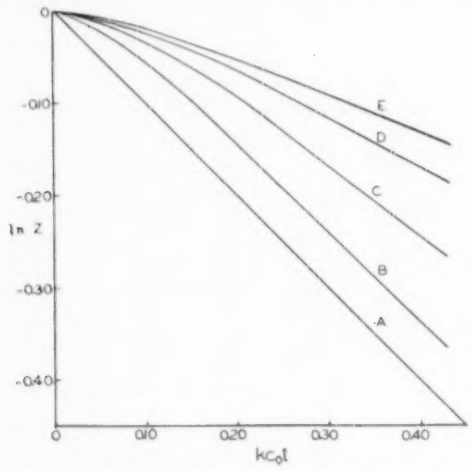


FIG. 1. *Ln Z vs.* kc_0t *for A, no diffusion effect; B,* $\delta = 1.0$*; C,* $\delta = 3.0$*; D,* $\delta = 7.0$*; E,* $\delta = 10.0$*.*

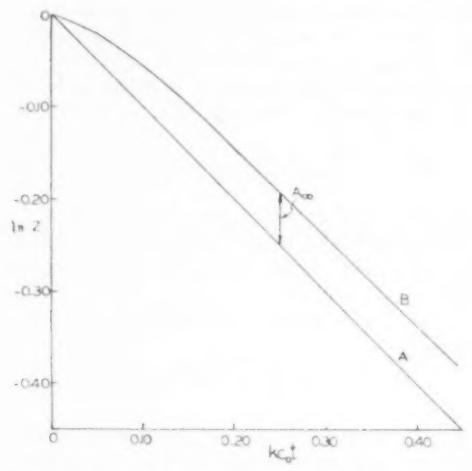


FIG. 2. *Ln Z vs.* kc_0t *for A, no diffusion effect; B,* $\delta = 1.0$*.*

TABLE III

VALUES OF A_∞ AS A FUNCTION OF δ

δ	A_∞ 1	2	3	4
0	0.0000	0.0000	0.0000	0.0000
1	0.0626	0.0632	0.0625	0.0598
3	0.1923	0.1947	0.1875	0.1794
5	0.3274	0.3338	0.3125	0.2990
7	0.4675	0.4801	0.4375	0.4186
10	0.6858	0.7102	0.6250	0.5980
15	1.0753			
20	1.4924			
30	2.3981			
50	4.4107			

1—From the numerical evaluation of equation (9).
2—From equation (16).
3—From equation (17).
4—From equation (17) using only the first root, β_1.

Or, using equation (15),

$$A_\infty = 2\delta \sum_{i=1}^{\infty} \frac{1}{\beta_i^2}. \qquad (17)$$

The values of A_∞ corresponding to various values of δ are tabulated in Table III, as expressed by the relationships in equations (16) and (17), as well as by the numerical evaluation of equation (9) at $t = \infty$, and by the approximation used by Reese and Eyring in which they considered only the first root of the Bessel function (columns 2, 3, 1, 4, respectively). The numerical evaluation of equation (9) may be considered as a reference. Values of A_∞ as evaluated from equation (16) for values of δ greater than 10 are not shown, since it was found that beyond this value of δ the series diverges.

Actually, recourse to equations (16) or (17) is not necessary when only the diffusion coefficient is to be determined, since the numerical evaluation of A_∞ for various values of δ (Table III, column 1) can be used for this purpose. That is, A_∞ and kc_0a^2 may be evaluated from experimental data as described above; the value of δ corresponding to A_∞ may be read from a plot describing this relationship, and D may be determined immediately. This procedure, of course, assumes that it has been established that diffusion is actually the process controlling the reaction.

Summary

The general equation for the kinetics of the successive processes of the relatively rapid diffusion of a reagent into a cylindrical fiber, followed by a bimolecular chemical reaction, has been developed and applied to the extent of the reaction and to the resulting decay of stress, based on the assumption of a linear relationship between stress and the extent of the reaction.

Two methods of solution of the equation have been indicated and a comparison is made with the solution of a similar problem as carried out by Reese and Eyring.

Finally, the authors have considered the method by which the parameters in this equation can be evaluated experimentally.

Acknowledgment

This work was conducted as part of the internationally supported Wool Research Project.* The authors are grateful to Prof. A. V. Tobolsky for many helpful discussions during the course of the mathematical analysis and in the interpretation of the results.

Literature Cited

1. Alexander, P., Carter, D., and Hudson, R. F., *J. Soc. Dyers and Colourists* **65**, 152 (1949).
2. Alexander, P., and Hudson, R. F., *J. Phys. Colloid Chem.* **53**, 733 (1949).
3. Andrews, R. D., Tobolsky, A. V., and Hanson, E. E., *J. Applied Phys.* **17**, 352 (1946).
4. Barrer, R. M., "Diffusion In and Through Solids," Cambridge, University Press, 1941.
5. Barrer, R. M., in "Symposium on Fibrous Proteins," Leeds, England, Soc. Dyers and Colourists, 1946, p. 108.
6. Boyd, G. E., Adamson, A. W., and Myers, L. S., Jr., *J. Am. Chem. Soc.* **69**, 2836 (1947).
7. Carslaw, H. S., and Jaeger, J. C., "Conduction of Heat in Solids," London, Oxford University Press, 1949, p. 179.
8. Collins, F. C., and Kimball, G. E., *J. Colloid Sci.* **4**, 425 (1949).
9. Crank, J., *Phil. Mag.* **39**, 140 (1948).
10. Crank, J., *Phil. Mag.* **39**, 362 (1948).
11. Crank, J., *J. Soc. Dyers and Colourists* **64**, 386 (1948).
12. Flory, P. J., *Chem. Revs.* **35**, 51 (1944).
13. Guth, E., and James, H. M., *J. Chem. Phys.* **11**, 455 (1943).
14. Hermans, J. J., *J. Colloid Sci.* **2**, 387 (1947).
15. Katz, S. M., and Tobolsky, A. V., TEXTILE RESEARCH JOURNAL **20**, 87 (1950).
16. Lundgren, H., manuscript in preparation.

* Sponsored by The Wool Bureau, Inc., acting for the International Wool Secretariat and the American Wool Council; the Office of Naval Research of the Navy Department, and a number of American wool manufacturers. Other phases of the project are being conducted under a Research and Marketing Act contract for the U. S. Department of Agriculture.

17. Menkart, J., and Speakman, J. B., *J. Soc. Dyers and Colourists* **63**, 322 (1947).
18. Mochulsky, M., and Tobolsky, A. V., *Ind. Eng. Chem.* **40**, 2155 (1948).
19. Neale, S. M., and Stringfellow, W. A., *Trans. Faraday Soc.* **29**, 1167 (1933).
20. Patterson, W. L., Geiger, W. B., Mizell, L. R., and Harris, M., *J. Research Natl. Bur. Standards* **27**, 89 (1941); *Am. Dyestuff Reptr.* **30**, 425 (1941); TEXTILE RESEARCH **11**, 379 (1941).
21. Reese, C. E., and Eyring, H., TEXTILE RESEARCH JOURNAL **20**, 743 (1950) (this issue).
22. Stern, M. D., and Tobolsky, A. V., *J. Chem. Phys.* **14**, 93 (1946).
23. Tobolsky, A. V., and Andrews, R. D., *J. Chem. Phys.* **13**, 3 (1945).
24. Tobolsky, A. V., Prettyman, I. B., and Dillon, J. H., *J. Applied Phys.* **15**, 380 (1944).
25. Treloar, L. R. G., *Trans. Faraday Soc.* **40**, 59 (1944).
26. Wall, F. T., *J. Chem. Phys.* **10**, 132 (1942).
27. Wall, F. T., *J. Chem. Phys.* **10**, 485 (1942).
28. Wilson, A. H., *Phil. Mag.* **39**, 48 (1948).

(Manuscript received July 13, 1950).

Correction

"Some Felting Properties of Wools of Different Geographical Origins," by Arnold M. Sookne, Herman Bogaty, and Milton Harris

In the paper of the above title in the September, 1950, TEXTILE RESEARCH JOURNAL, the conditions under which the measurements of mechanical and frictional properties of single fibers were made were inadvertently omitted. These measurements were all made with the fibers immersed in water at 70° F.

The Kinetics of Wool Dyeing

Part II: The Adsorption of Surface-Active Dyes by Wool and Other Fibers*

P. Alexander and D. A. Charman

Department of Physical and Inorganic Chemistry, Imperial College of Science, London

Abstract

The kinetic curves for the adsorption on textile fibers of a dye having a long hydrocarbon chain (Carbolan Crimson BS) indicate that there is an initial rapid, but limited, reaction which is followed by a much slower reaction. The influence of electrolytes, dye concentration, and temperature was studied, and the magnitude of the initial adsorption was correlated with the surface activity of the solution. The dye thus taken up was shown to be located on the fiber surface which, being largely nonpolar, is an interface for adsorption of surface-active substances. It is suggested that the surface activity of the dye contributes substantially to its high anion affinity.

THE ANION of an acid dye may enter a fiber in two different ways [4]. Firstly, fibers containing positively charged groups (*e.g.*, proteins on the acid side of the isoionic point) will hold the dye ion as a gegenion which is not replaced by inorganic ions such as chloride or sulfate because the complex organic anion possesses a very much greater affinity for the fiber. The acid-dyeing of wool can be represented as an anion-exchange reaction where the dye replaces the anion of the inorganic acid. Secondly, dyes with very great anion affinity can be sorbed by uncharged fibers as leading or potential-determining ions, and in this case the inorganic cation becomes the gegenion. The dyeing of cotton with direct colors and the neutral dyeing of wool proceeds in this way. There is no sharp dividing line between dyes of anion affinity sufficient only to replace simple ions as gegenions and dyes with an anion affinity great enough to become leading ions, the difference being one of degree.

Dispersive forces were shown to play an important part in anion affinity by Steinhardt, Fugitt, and Harris [15], who demonstrated that the affinity of an acid for wool increases with the size of the anion. Kitchener and Kressman [10] showed a similar effect for cation resin exchangers with a series of substituted ammonium salts. Hydrogen bonds have been postulated as being responsible for the fixation of dyes by cotton [11, 16, 17], and with many dyes this may be one of the most important factors contributing to high anion affinity. The different hydrogen-bond behavior of different fibers possibly explains why some dyes which are excellent for cotton, say, are of poor fastness on wool, and vice versa. It will be shown in this paper that surface activity is another factor contributing to anion affinity, and that some dyes are adsorbed very strongly because they are attracted to the fiber interface, which is less polar than the aqueous dye solution.

The rate of dyeing is controlled either by diffusion through the solution to the fiber surface, when it is dependent on stirring, or by diffusion through the fiber, which requires a greater activation energy [3]. Dyes of high affinity, such as the neutral-dyeing wool colors, consist of large molecules, which in many cases are aggregated to form still larger units, which diffuse very slowly into fibers at room temperature; as a result, the rate of dyeing becomes constant and independent of increases in agitation at low stirring speeds. With some of these dyes a small and limited

* Part I of this series appeared in the July, 1950, issue, page 481.

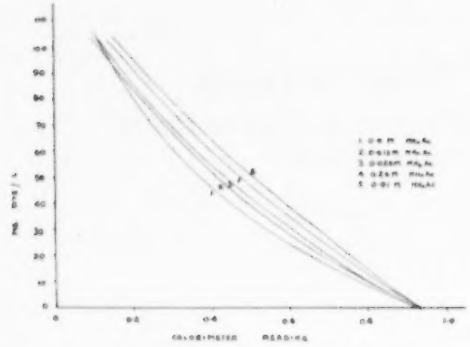


FIG. 1A. *Variation of extinction coefficients of Carbolan Crimson dye solution containing different concentrations of ammonium acetate as determined with a Spekker colorimeter.*

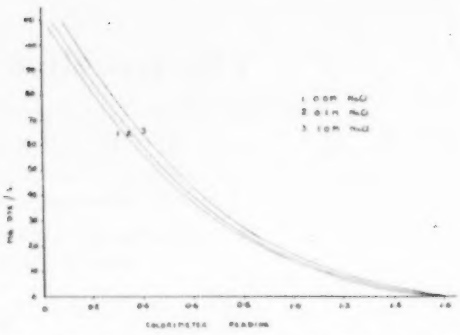


FIG. 1B. *Variation of extinction coefficients of Sky Blue FF dye solutions containing different concentrations of sodium chloride as determined with a Spekker colorimeter.*

rapid initial uptake of dye could be detected which, when complete, was followed, at room temperature, by the very slow diffusion into the fiber. The dye taken up initially was shown to be located on the fiber surface, and the amount of surface adsorption was determined from the rate-of-dyeing curves. The initial sorption was very dependent on stirring, unlike the subsequent fiber diffusion, and the break in the curve can best be identified in a well-agitated system, where the differences in rate of the two processes are accentuated. The effect was most pronounced with surface-active dyes, and was therefore studied in detail with Carbolan Crimson BS (Imperial Chemical Industries Ltd.), which consists of the simple acid dye Azo Geranine 2GS (C. I. No. 637) with one or more long hydrocarbon chains attached [6].

Experimental Procedure

Measurement of Dye Uptake

Fabric was purified by extraction with water, alcohol, and ether and the several dyes used were freed from added electrolytes by recrystallization or precipitation. The experiments were carried out in a conical flask, with shaking by hand in a thermostat. The amount of adsorption is independent of the solution-to-fabric ratio, and the low ratio of 25 : 1 was used to ensure an accurately measurable change in dye concentration. Estimation of solution dye content was made with a Spekker colorimeter; separate calibration curves had to be constructed for solutions of the same dye containing different concentrations of added salts because the extinction coefficient of many dyes, including Carbolan Crimson, is reduced by electrolytes (see Figure 1). The extinction coefficients of simple acid dyes such as Orange II and Azo Geranine are not changed by salts. When wool dyeing was done for long periods at elevated temperatures, protein decomposition products went into the solution, thereby changing its color value, and an accurate colorimetric estimation of the dye content of the solution was impossible. This difficulty was not encountered in this work because no such decom-

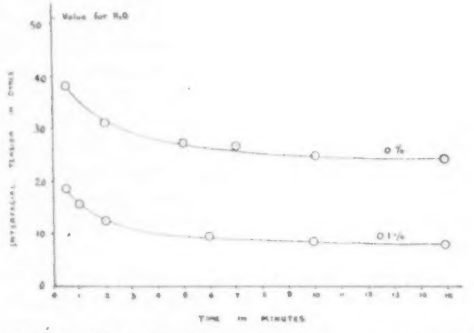


FIG. 2. *Variation in interfacial tension with time as calculated from drop size of a 0.02% Carbolan Crimson solution containing (1) no salt, and (2) 0.1% ammonium acetate (against petroleum ether).*

position occurs at the low temperatures used. Ammonium acetate was chosen as the electrolyte for most of the experiments because it buffers the solution to pH 7 and therefore excludes the possibility of dyeing by ion-exchange.

For the construction of a kinetic-dyeing curve, a different experiment was carried out for each point (*i.e.*, for each different time). With Carbolan Crimson, fiber diffusion at room temperature can be neglected since it is very slow compared with surface adsorption, which, with hand-shaking, was complete in 2 to 3 min., and the amount of dye taken up after 3 min. was therefore considered in this investigation to be the amount of initial adsorption (see Figure 3).

Determination of Surface Tension of Dye Solutions

The drop-size method, using an "Agla" (Burroughs Wellcome) micrometer syringe, was employed [1]; the capillary was calibrated with water at 22°C. For the interfacial-tension measurements petroleum ether, b.p. 110°C, was used. The establishment of equilibrium is slow and misleading results are obtained if this is not taken into consideration. The following procedure was adopted. The micrometer was turned slowly until the drop formed fell off. After this a drop was set up, not necessarily slowly, having a volume of 2% less than the previous one, and the time for the drop to fall was measured. This process was continued until a drop size was attained such that the drop did not fall off in 15 min.; the interfacial-tension value at this point (15 min. falling time) was taken as the surface tension for the air-solution interface and as the interfacial tension for the petroleum-solution interface because the hyperbolic curve relating the tension and time had flattened out (see Figure 2 for typical examples).

Results and Discussion

1. Evidence for Surface Adsorption

The kinetic curve for dyeing wool at 25°C with Carbolan Crimson in a solution of ammonium acetate (Figure 3) clearly shows an initial rapid adsorption, followed by a much slower process which continues until equilibrium is reached (24 hrs.). In contrast, it is seen that the curve for Azo Geranine GS (Figure 4) is continuous and is similar to those for other simple acid dyes—Orange II (C. I. No. 151) or Acid Orange GG (C. I. No. 27). In all cases, at neutrality there is little adsorption in the absence of salt but adsorption is increased by the addition of ammonium acetate, since the cation aids dyeing by the common-ion effect. Carbolan Crimson has a very great affinity for wool, even at neutrality, but only in the presence of electrolyte; the dye-bath exhaustion is so great that no dye can be detected colorimetrically in the solution at equilibrium.

In order to relate the initial adsorption to the presence of a long hydrocarbon chain in Carbolan Crimson, the rate of dyeing of other dyes of high affinity—*e.g.*, Sky Blue FF (C. I. No. 578), Coomassie Milling Scarlet (C. I. No. 443), Benzo Purpurine 4B (C. I. No. 448), and Polar Yellow R—

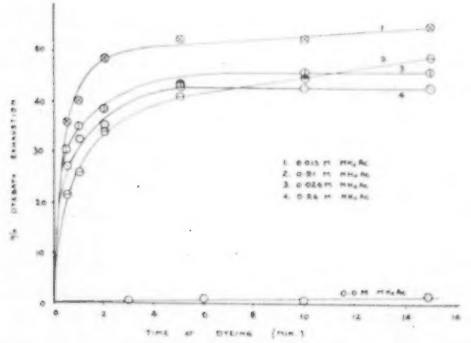


FIG. 3. *Rate of dyeing of wool at 25°C with a solution of 75 mg./l. of Carbolan Crimson, containing different concentrations of ammonium acetate at a solution-to-fiber ratio of 25:1.*

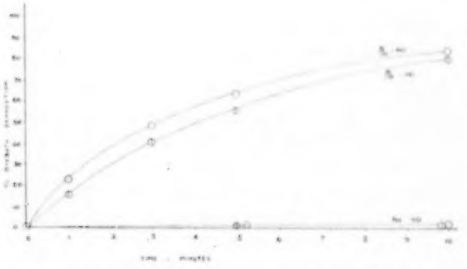


FIG. 4. *Rate of dyeing with Azo Geranine GS (200 mg./l.) at 25°C and a solution-to-wool ratio of 25:1. Dye only (⊙——⊙); with 1% ammonium acetate (①——①) (at neutrality and in N/100 HCl).*

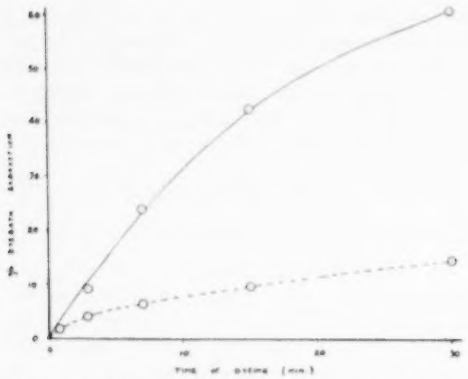


FIG. 5. *Rate of dyeing with Coomassie Milling Scarlet (⊙——⊙) and Sky Blue FF (⊙-----⊙) with wool at 25°C. Dye concentration 100 mg./l.; ammonium acetate concentration 0.026M; solution-to-wool ratio 25:1. No dye sorbed in absence of ammonium acetate.*

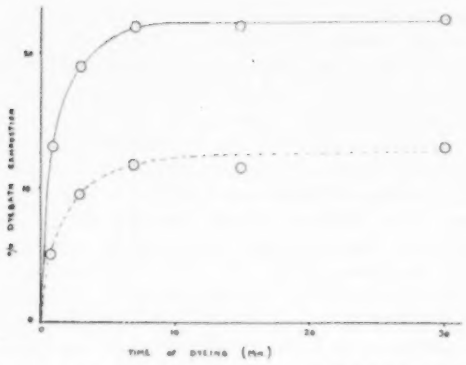


FIG. 6. *Rate of dyeing of wool with Carbolan Yellow (⊙——⊙) and Carbolan Violet (⊙-----⊙) in the absence of added electrolyte. Dye concentration 200 mg./l.; temperature 25°C; solution-to-fiber ratio 25:1.*

was followed. These dyes possess no hydrocarbon chains and the first two (Figure 5) give smooth kinetic curves and the last two react so slowly at room temperature that the amount sorbed in 30 min. is within experimental error. However, other Carbolan dyes possessing long hydrocarbon chains show pronounced initial adsorption even in the absence of electrolytes (Figure 6). In addition, the property is a general one—*i.e.*, Carbolan Crimson behaves similarly with cotton and nylon (Figure 7). Cotton adsorbs Carbolan Crimson even in the absence of salts, but the quantity of dye adsorbed is greatly increased in the presence of salts, reaching a limiting value which is ten times that for wool; this can be seen by comparing Figures 7 and 11.

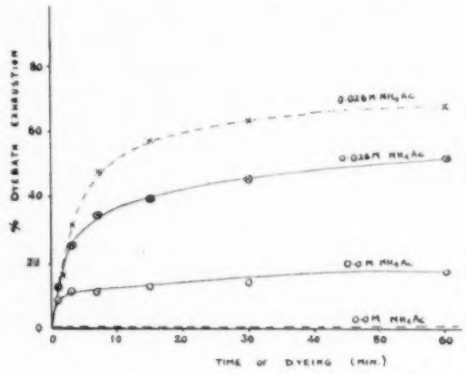


FIG. 7. *Rate of dyeing with Carbolan Crimson on cotton (——) and nylon (-----), 25°C, dye concentration for cotton 500 mg./l. and for nylon 200 mg./l., both at a solution-to-fiber ratio of 50:1.*

2. Effect of Temperature and Concentration of Dye and Ammonium Acetate

Initial adsorption is clearly evident at 0°C, 25°C, and 50°C but not at 75°C (see Figures 3, 8–10). The effect of changing the dye concentration on the rate curve is shown in Figure 11 in terms of percentage dye-bath exhaustion; the lower the concentration the greater the exhaustion. The actual quantity of dye adsorbed does not, of course, decrease with increasing concentration; only the ratio of dye on the fiber to dye in solution decreases.

Figures 3, 9, 10, and 11, together with experiments discussed in section 4, clearly demonstrate that all the dye which can be adsorbed on the surface in equilibrium with the dye in solution is taken up under the conditions of experiment within 3 min. at 25°C and 50°C, although at 0°C the process takes longer. Adsorption isotherms can therefore be constructed (see Figures 12 and 13), and the quantity of dye on the fiber, calculated from the exhaustion of the dye bath, is plotted against the dye-bath concentration at the end of the 3-min. initial reaction period. It is seen that at 0°C (Figure 8) and 25°C the optimum salt concentration is approximately 0.1%, although at 50°C the dye uptake increases

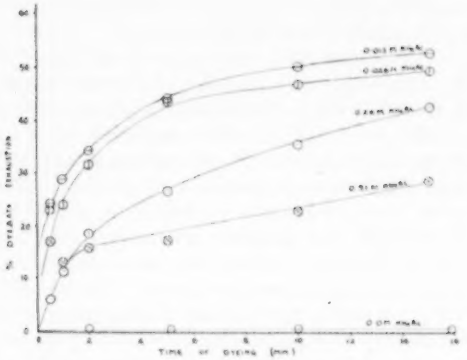


FIG. 8. *Rate of dyeing of wool with Carbolan Crimson (75 mg./l.) and different amounts of ammonium acetate at 0°C.*

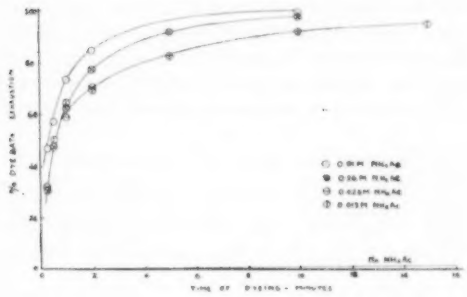


FIG. 10. *Rate of dyeing of wool with Carbolan Crimson (75 mg./l.) and different amounts of ammonium acetate at 75°C.*

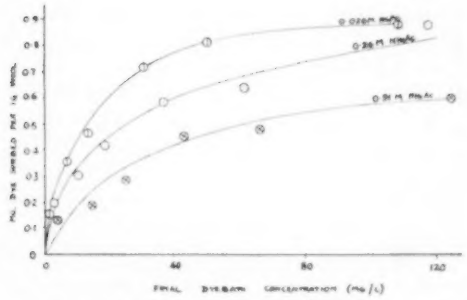


FIG. 12. *Change of initial adsorption with dye-bath concentration at different ammonium acetate concentrations; temperature 50°C.*

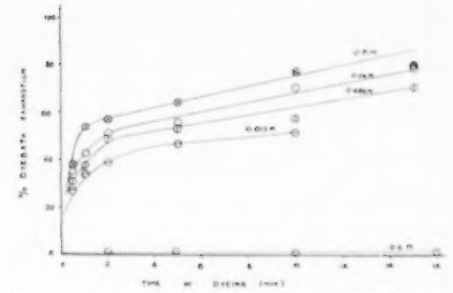


FIG. 9. *Rate of dyeing of wool with Carbolan Crimson (75 mg./l.) and different amounts of ammonium acetate at 50°C.*

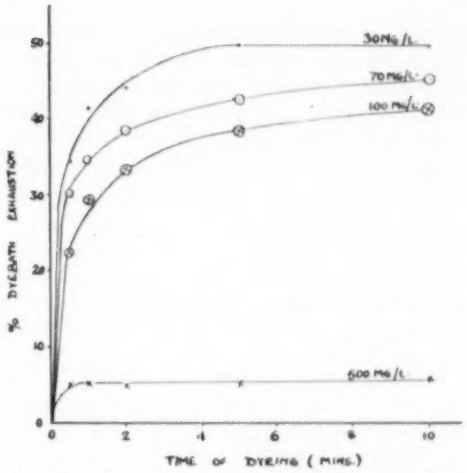


FIG. 11. *Rate of dyeing of wool with Carbolan Crimson solutions of different initial concentrations, temperature 25°C, solution-to-wool ratio 25:1, concentration of ammonium acetate 0.2% for each experiment.*

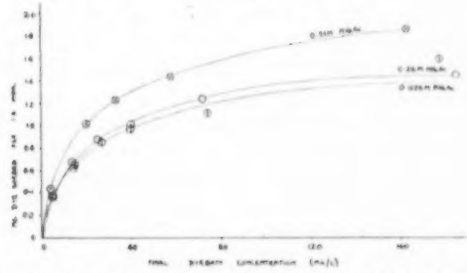


FIG. 13. *Change of initial adsorption with dye-bath concentration at different ammonium acetate concentrations; temperature 25°C.*

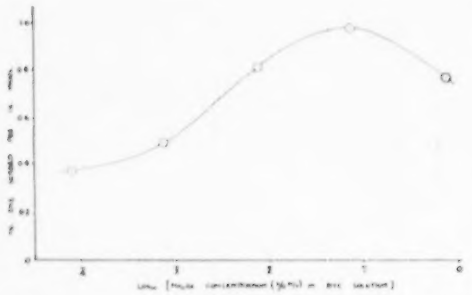


FIG. 14. *Relationship between initial adsorption of Carbolan Crimson (150 mg./l.) and ammonium acetate concentration at 25°C.*

continuously with ammonium acetate concentration. This is discussed on page 769. In the absence of salt, no dye is adsorbed, although very small quantities of electrolyte bring about surface adsorption, as can be seen from Figure 14, in which a logarithmic abscissa is used to accommodate the wide range of concentration.

3. Effect of Electrolytes

The addition of salts has a very great influence on the surface properties of paraffin-chain salts [12], and the ion of opposite charge is primarily responsible.

Different electrolytes were used in order to determine the effect of anion and cation size and charge on the initial adsorption of Carbolan Crimson. The experiments were complicated owing to the fact that the dye precipitated at a critical concentration of the electrolyte employed. With a dye solution of 200 mg./l., precipitation occurred with different salt types as follows: A^+B^- (strong), 0.1*M*; $(2A^+)B^{--}$ (strong), 0.05*M*; A^+B^- (partly hydrolyzed—*e.g.*, ammonium acetate), 1.0*M*; $A^{++}(2B^-)$, $5 \times 10^{-3}M$; $A^{+++}(3B^-)$, $10^{-3}M$. The initial adsorption was found to be independent of the size of the cation and the size and valency of the anion. Thus, a constant adsorption of approximately 0.9 mg. of dye per g. of wool from a 140 mg./l. Carbolan Crimson solution at 25°C was obtained on the addition of the following salts: (*a*) 0.05M LiCl, NaCl, KCl, NH_4Cl, (*b*) 0.05*M* NaF, NaCl, NaBr, NaI, $NaNO_3$, and 0.025*M* Na_2SO_4. These results differ from those found by Aickin [2] on sorption of an alkyl sulfate by wool, where the influence of the cations of different monovalent salts followed a lyotropic series.

On the other hand, the valency of the cation affects the sorption considerably. Thus, with a solution of 150 mg./l. Carbolan Crimson and $10^{-3}M$ $Al_2(SO_4)_3$ a typical initial adsorption curve was obtained; 0.9 mg. dye/g. wool was adsorbed, in contrast to 0.35 mg./g. wool with $10^{-3}M$ KCl. With greater concentrations of $Al_2(SO_4)_3$ (*e.g.*, $10^{-4}M$) the dye bath is almost exhausted within 3 min., and it seems probable that the Al^{+++} is sorbed by the wool and the dye is then precipitated within the fiber.

Dye adsorption does not attain a maximum at an intermediate salt concentration with strong electrolytes and the amount of surface adsorption is the same with 0.05*M* and 0.1*M* KCl (*i.e.*, the highest concentration which does not produce precipitation); in this respect these salts differ from ammonium acetate.

The addition of sucrose urea and the anion-active agent cetyl sodium sulfate brought about no surface adsorption of dye by wool, and it would thus seem that only electrolytes have this property and then only if they are not themselves surface-active.

4. Diffusion of Adsorbed Dye into the Fiber

The adsorbed dye is readily removed by distilled water immediately after adsorption without intermediate drying, and it was found that a true re-

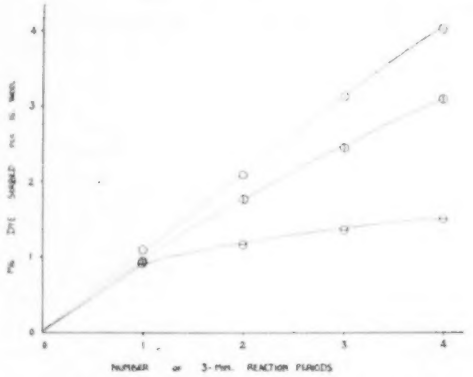


FIG. 15. *Effect of steaming (⊙), drying (ⓘ), and leaving in air for 15 min. (⊖) on the adsorption of dye in repeated 3-min. reaction periods. Dye-bath concentration 150 mg./l., ammonium acetate 0.2%, temperature 25°C.*

versible equilibrium exists for desorption. The resistance to washing of the adsorbed dye is greatly increased by drying, which suggests that the dye migrates into the interior of the fiber during the aftertreatment; the effectiveness of different methods of drying are compared in Table I. In addition, after such treatments the fibers were capable of adsorbing rapidly the same quantity as in the prior treatment. If, however, the fabric is merely left at room temperature for 15 min., very little dye is adsorbed in a subsequent treatment (see Figure 15). To eliminate the possibility that this effect is due to changes in the fiber structure on steaming and drying, adsorption experiments were performed on samples which had previously been steamed and dried. It can be seen from the first 3 min. of dyeing (Figure 15) that the quantity of dye adsorbed was not increased by these treatments.

As a check on the above results the dye content of the wool was determined by measuring the light reflected from the wool sample with a selenium-cell reflectometer (Evans Electroselenium Ltd.) and comparing with samples dyed at 100°C with solutions containing different amounts of Carbolan Crimson and 0.2% ammonium acetate. At 100°C the dye bath was completely exhausted within a few minutes and the amount of dye left in solution was too small to be detected. In every case the color intensity of a sample of wool with adsorbed Carbolan Crimson was less than that of a conventionally (*i.e.*, at 100°C) dyed sample. Immediately after the adsorption and while the sample was still wet, the light adsorption of the wool was 30–40% less than that of a wet sample dyed at 100°C and containing the same quantity of dye. After drying, the light adsorption of the adsorbed dye was about 25% less, whereas after steaming there was no difference. The color intensity of wool dyed with adsorbed dye was in every case increased by steaming to that of a sample dyed by the conventional method at the boil, but no change takes place when a dry sample is heated even for long periods. An exactly similar change in color intensity occurred on drying or steaming cotton and nylon samples which had sorbed Carbolan Crimson.

5. Surface Tension of Dye Solutions

These measurements are expressed to the nearest dyne only because the equilibrium value was considered to be that at which a drop did just not fall off (drop-size method), and Figure 2 indicates that this value is correct at best to within 1 dyne. Of all the dyes examined only the Carbolans lower the surface tension (air-solution interface) appreciably, and the addition of ammonium acetate has relatively little effect. The interfacial tension (petroleum-solution interface) of Carbolan Crimson against a hydrocarbon is greatly decreased by the addition of electrolyte, whereas for solutions of Carbolan Violet it is very low even in the absence of electrolyte.

Dyes which do not show rapid initial adsorption onto fibers do not lower the surface tension of water but they are able to reduce the interfacial tension. This is lowered to half by Carbolan Crimson in the absence of added electrolyte and by Polar Yellow solutions, although neither showed surface adsorption. The interfacial tension is, however, very greatly decreased by Carbolan Crimson with salt, and it appears as if it must be lowered to 10 dynes before adsorption onto wool will take place.

These results (see Table II) are in agreement with those of Gibby and Argument [8], who found that neither aggregated nor molecularly dispersed dyes were adsorbed at an air-water interface.

Conclusions

The following observations support the contention that the dye sorbed initially is located entirely on

TABLE I. EFFECT OF DIFFERENT AFTERTREATMENTS ON THE FASTNESS OF ADSORBED DYE

	(Dye adsorbed = 0.83 mg./l.) Mg. of dye*/g. of wool desorbed in 10 min. in:		
Aftertreatment	(Water at 25°C)	(Water at 100°C)	(1% Soap soln. at 100°C)
None; 15 min. after adsorption	0.44	0.42	0.78
Standing for 24 hrs. at 25°C	0.12	0.19	0.40
In air-oven at 80°C for 2 hrs.	0.05	0.14	0.31
In air stream at 110°C for 10 min.	0.12	0.20	0.52
In steam at 100°C for 10 min.	0.0	0.0	0.05

* Carbolan Crimson.

TABLE II. SURFACE AND INTERFACIAL TENSION OF DYE SOLUTIONS AT 22°C

Solution	Tension (dynes) Against petroleum ether	Against air
Water only	51	
1% ammonium acetate	49	
0.02% Carbolan Crimson	24	44
0.02% Carbolan Crimson + 0.005% ammonium acetate	20	
0.02% Carbolan Crimson + 0.01% ammonium acetate	11	
0.02% Carbolan Crimson + 0.02% ammonium acetate	12	
0.02% Carbolan Crimson + 0.1% ammonium acetate	8	
0.02% Carbolan Crimson + 0.2% ammonium acetate	8	36
0.02% Carbolan Crimson + 1% ammonium acetate	8	
0.02% Carbolan Crimson + 2% ammonium acetate	8	40
0.02% Carbolan Crimson + 0.1% potassium chloride	6	
0.005% Carbolan Crimson	31	
0.005% Carbolan Crimson + 0.2% ammonium acetate	9	
0.05% Carbolan Crimson	14	
0.05% Carbolan Crimson + 0.2% ammonium acetate	9	
0.1% Carbolan Crimson	10.8	47
0.1% Carbolan Crimson + 0.2% ammonium acetate	9	40
0.02% Carbolan Violet	6	
0.02% Carbolan Violet + 0.2% ammonium acetate	7	
0.02% Azo Geranine	45	79
0.02% Azo Geranine + 0.1% ammonium acetate	46	
0.02% Azo Geranine + 1% ammonium acetate	45	
0.02% Polar Yellow	25	80
0.02% Polar Yellow + 0.1% potassium chloride	23	
0.02% Sky Blue FF	48	
0.02% Sky Blue FF + 0.1% potassium chloride	48	78
0.02% Sky Blue FF + 0.5% potassium chloride	40	
0.02% Benzopurpurine	48	81
0.02% Coomassie Milling Scarlet	45	78

the surface of the fibers: (1) The dye is readily and completely removed by cold water, although on heating or steaming it becomes fixed and very difficult if not impossible to remove with water. (2) After steaming, wool can adsorb a further quantity of dye even though the fiber had been apparently saturated with respect to that dye solution. (3) The quantity of Carbolan Crimson required to saturate the fiber at neutrality [13] is about 200 times greater than that adsorbed in the initial reaction. (4) Even at room temperature very much larger quantities than that adsorbed initially can be taken up, although the reaction will take a comparatively long time.

The very slow reaction following the initial adsorption process represents diffusion from the surface into the fiber, and fixation by heat or steam promotes this migration of dye, leading to a more even distribution of dye in the fiber. Since the quantity of dye held on the surface is very small when compared with the total capacity of the fiber, the surface will be far from a state of saturation after a leveling process such as steaming, and the amount of dye adsorbed after fixation will therefore be almost as great as that adsorbed by an undyed fiber. The failure to detect surface adsorption at 75°C arises from the fact that the temperature coefficient for fiber diffusion is twice that for the liquid diffusion which governs the supply of dye to the surface [3], so that at high temperatures the surface never becomes saturated.

It seemed possible that the surface adsorption of dyes is related to the aggregation of dye molecules in solution since both effects are increased by addition of salts, decreased at high temperatures, absent with Azo Geranine, and great with Carbolan Crimson. Recent experiments [5], however, in which the molecular sizes of dyes were determined by light-scattering, showed that the effects were not exceptionally great in the case of Carbolan Crimson. Previous measurements in this laboratory based on diffusion through a porous sintered-glass membrane were invalid because of interference caused by adsorption of the dye on the glass. The molecular size of Carbolan Crimson in dilute salt solutions is less than that of Polar Yellow, Benzopurpurine, and Coomassie Milling Scarlet, none of which show surface adsorption: aggregation is therefore unlikely to play an important part in this phenomenon.

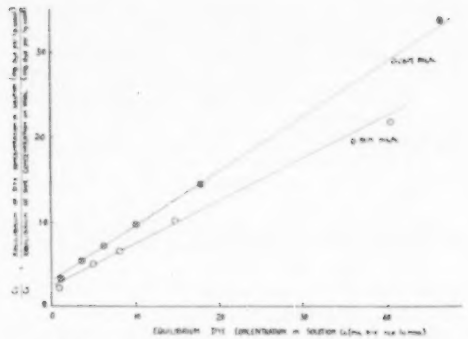


FIG. 16. *"Langmuir plot" for adsorption of Carbolan Crimson by wool at 50°C in the presence of ammonium acetate of different concentrations.*

The parallelism between interfacial tension and initial adsorption indicates that the latter is an effect which is attributable to the surface activity of the dye solutions. Wool is hydrophobic, with large nonpolar areas [7], and a surface-active material in aqueous solution will concentrate at the fiber surface and produce the effect of rapid adsorption provided that the diffusion within the fiber is slow compared with the rate of transport through the liquid. It is very difficult to measure interfacial tension between a liquid and a solid, and the surface activity of the dye solution and fiber must hence be deduced from the value in another system where it can be determined. Petroleum ether, although unlike wool, simulates it more closely than air, and this explains why the interfacial tension represents surface adsorption behavior more closely than does surface tension against air.

The cations of the added electrolyte act as gegenions and decrease the repulsion between the long-chain anions, enabling a higher concentration to be maintained at an interface and more dye to be taken up on the fiber surface. The influence of salts on the surface concentration of Carbolan Crimson depends on the nature of the interface; thus, ammonium acetate has a relatively slight effect on the surface tension but a considerable effect, even at low concentrations, on the interfacial tension with petroleum ether and, by analogy with the dyeing data, with the fiber.

The adsorption of dye is greatest at a concentration of 0.1-0.2% ammonium acetate, but no such maximum is observed with potassium chloride or shown by the interfacial tension of the solutions. It seems probable that ammonium acetate, which is known to have greater affinity [14] for proteins than chloride, begins at high concentrations to compete with Carbolan Crimson for the available sorption sites. At lower concentrations the ammonium ion acts as a gegenion only and promotes adsorption like potassium chloride does.

Cotton adsorbs Carbolan Crimson even in the absence of electrolytes, and in their presence adsorbs it much more readily than wool does. Cotton, which swells more than wool, has a greater available surface, so that even when the surface concentration of Carbolan Crimson is small, a measurable quantity of dye is removed from solution. Carbolan Violet has a low interfacial tension (*i.e.*, a high surface concentration) even in the absence of electrolyte, and this explains why the pure dye is readily adsorbed.

The adsorption isotherms for Carbolan Crimson in the presence of electrolytes, when plotted as $\frac{\text{(concentration in solution)}}{\text{(concentration in fiber)}}$ against concentration in solution, give straighter lines (Figure 16) than a plot of log (dye on fiber) against log (dye in solution). The surface adsorption of dye is therefore of the Langmuir type, from which it follows that the sorption sites are all of equal energy and are limited in number. In view of this it seems probable that Carbolan Crimson is sorbed by the main polypeptide chain and not by the basic side groups, which are very diverse and would not all be of the same energy.

The very much greater affinity of Carbolan Crimson as compared to Azo Geranine for wool and other fibers must be related to the hydrocarbon chain of Carbolan Crimson since this is the only difference between the two dyes. It has generally been assumed that hydrogen bonds are the major factor in the affinity of anions which can dye neutral wool and cotton, but such links can play no part in the affinity of Carbolan Crimson because paraffin chains have no mobile hydrogen atoms. The increase in affinity of Carbolan Crimson over Azo Geranine is entirely due to the van der Waals' attraction between the dye and the fiber and to the surface activity which produces positive adsorption on the large internal surface of the fiber. It is impossible to separate quantitatively the influence of these two factors, but it seems probable that the surface-adsorption effect plays the more important part.

Although the addition of a C_{12} to C_{16} hydrocarbon chain would increase the affinity of Azo Geranine anion, the increase, if due to van der Waals' forces only, would not be expected to be of the magnitude actually observed for Carbolan Crimson. This point is supported by the work of Gilbert [9], who determined the contribution which is due wholly to the dispersive forces of a benzene ring to the affinity of a dye anion for wool.

Acknowledgment

The authors wish to thank Messrs. Wolsey Ltd., Leicester, for the financial support which made this investigation possible, and Prof. H. V. A. Briscoe for his help and interest.

Literature Cited

1. Adam, N. K., "The Physics and Chemistry of Surfaces," London, Oxford University Press, 1941, p. 376.
2. Aickin, R. G., *J. Soc. Dyers and Colourists* **60**, 60 (1944).
3. Alexander, P., Gough, D., and Hudson, R. F., *Trans. Faraday Soc.* **45**, 1058 (1949).
4. Alexander, P., and Kitchener, J. A., TEXTILE RESEARCH JOURNAL **20**, 203 (1950).
5. Alexander, P., and Stacey, K., unpublished data.
6. Bird, C. L., "The Theory and Practice of Wool Dyeing," Soc. Dyers and Colourists, Bradford, England, 1947.
7. Cassie, A. B. D., and Baxter, S., *Trans. Faraday Soc.* **40**, 546 (1944).
8. Gibby, C. W., and Argument, C., *J. Chem. Soc.* **1940**, 596 (1940).
9. Gilbert, G. A., *Proc. Roy. Soc.* **183A**, 167 (1944).
10. Kitchener, J. A., and Kressman, T. R. E., *J. Chem. Soc.* **1949**, 1208 (1949).
11. Marshall, W. J., and Peters, R. H., *J. Soc. Dyers and Colourists* **63**, 446 (1947).
12. Powney, J., and Addison, C. C., *Trans. Faraday Soc.* **33**, 1243 (1937).
13. Skinner, B. G., and Vickerstaff, T., *J. Soc. Dyers and Colourists* **61**, 193 (1945).
14. Smith, E. J., *J. Biol. Chem.* **113**, 473 (1936).
15. Steinhardt, F., Fugitt, C. H., and Harris, M., *J. Research Natl. Bur. Standards* **26**, 293 (1941).
16. Valko, E., "Colloid Chemistry," New York, Reinhold Publishing Co., 1946, vol. 6, p. 594.
17. Willis, H. F., Warwicker, J. O., Standing, H. A., and Urquhart, A. R., *Trans. Faraday Soc.* **41**, 506 (1945).

(*Manuscript received April 24, 1950.*)

Letters to the Editor

The Relationship of Wax Content to Maturity of Cotton

School of Textiles,
The Clemson Agricultural College
Clemson, South Carolina

June 27, 1950

To the Editor
Textile Research Journal

Dear Sir:

In a paper presented at a meeting of The Fiber Society at Clemson College in April, 1949, and in a subsequent Letter to the Editor of Textile Research Journal, which was printed in the November, 1949, issue, "Relationship of Wax Content to Maturity of Cotton" [1], it was shown that a relation exists between percent wax in cotton fibers and fiber maturity and that it is possible quantitatively to explain this relationship by relating the percentage of wax to the specific surface of the fiber (surface area per unit weight) or the reciprocal wax percentage to the amount of cell-wall material per unit surface ("average maturity" *). A linear proportionality was found to exist between these quantities. These findings were disclosed in a study of maturity using chemical methods.

Marsh, Barker, Kerr, and Butler in a subsequent article, in the Textile Research Journal of May, 1950 [2], apply the same principle in a study of the wax content of *different varieties* of cotton of the *same maturity*. Relating the percent of wax with the specific surface in the different varieties, they also found a close correlation between the two quantities and conclude that the amount of wax per unit surface is the same for all different varieties.

It is indeed gratifying that their results coincide so closely with the principles and results of the article on maturity.

However, these authors, in a Letter to the Editor, dated January 6, 1950 [3], bring to attention a few points of the article on maturity which might tend to obscure its main points and intention as given above. Although these points are of minor importance and do not interfere with the main trend of the article on maturity or the complete agreement of the two articles in principle and major points, a short discussion of the points in their letter may be helpful.

Their main point refers to the *application* of the wax-maturity relationship found for the measurement of the "average maturity," in that they state that the same quantity (namely, specific surface) may also be measured from arealometer determinations, which are easier to make. This is true (if it is accepted that the arealometer measures specific surfaces in all circumstances) and this fact was never disclaimed in the article in question; in fact, the disadvantages of the wax determinations as compared with the *physical methods* have been emphasized from the beginning (see the last paragraph, "Prospects of Developing New Methods for Practical Determination of Average Maturity") [1]. The main purpose of applying the wax relationship as a basis for maturity measurements was simply to *approach the problem of maturity from a chemical angle*, and it was pointed out that the original wax method might have value only for special laboratory purposes or for routine determination in case simpler and quicker methods might be based on it. This was stated in the following words:

"The special relationship between wax content and average maturity established in these studies will in itself be of considerable interest" and "the question arises whether or not on the basis of the results ob-

* In these studies of maturity, the reciprocal value of the specific surface was termed "average maturity," as it denotes the amount of cell-wall material, depending on the degree to which the average fiber material has matured in a definite variety.

tained it would be possible to develop a new practical method. It might be possible to adapt the wax method described above to practical use or, alternatively, to employ a determination of the pectins or perhaps other substances, which might require less time."

Special consideration should be given, however, to one point brought out by the above authors—namely, that their experimental data indicated the wax per unit area to be influenced by the weathering of cotton, and that the wax method would be principally unsuitable for the determination of maturity. The data given, however, refer to an unusually long period of weathering (over 11 weeks) and even in this case the resulting average *increase* in wax percentage is not more than 10%. It must be granted that if the method were to be used for routine determinations, in cases of cottons of completely unknown origin (which might have been exposed to such severe weather conditions) this margin would have to be taken into account, but then the same objection would also hold for all other methods that determine the ratio of surface to fiber weight, *including the arealometer method*. This is because not the wax but rather other substances, presumably cellulose and water-soluble materials, are reduced in weathering (which explains why the authors found an *increase* in percent of wax after weathering). This change in ratio of substances to surface area means a change in the specific surface and will be shown up no matter what method is used for its determination (whether wax, arealometer, or other methods).

Their other point that the terms "perimeter" and "surface area" * were used in the article in a loosely interchangeable manner would be justified had their use been in connection with different varieties, which in turn would have involved differences in perimeter. These terms as used in the article refer only to the maturity variation *within each single variety* and in that case are related to each other by a fixed proportionality factor, genetic differences in perimeter between different varieties playing no part. Under such circumstances it is of no importance which of the terms is used.

In conclusion, it is believed, as stated in the original article, that the wax-maturity relationship is of fundamental interest in studies of wax content of cotton in general and also offers a possibility for a chemical approach to maturity problems in laboratory research, but is not intended as such for routine determinations of maturity, unless a quicker method might be based on it (or on the underlying theorem).

Literature Cited

1. Heyn, A. N. J., Relationship of Wax Content to Maturity of Cotton. Paper presented at the meeting of The Fiber Society, Clemson, S. C., Apr. 12, 1949; and Letter to the Editor, TEXTILE RESEARCH JOURNAL **19**, 711 (Nov. 1949).
2. Marsh, P. B., Barker, H. D., Kerr, T., and Butler, M. L., Wax Content as Related to Surface Area of Cotton Fibers, TEXTILE RESEARCH JOURNAL **20**, 288 (May 1950).
3. Marsh, P. B., Barker, H. D., Kerr, T., and Butler, M. L., Wax Content of Cotton Fibers (Letter to the Editor), TEXTILE RESEARCH JOURNAL **20**, 297 (May 1950).

A. N. J. HEYN

* The term "surface" has been used in the pure mathematical sense in the article.

INDUSTRIAL SECTION

Use of Tabulator Data in the Analysis of Sliver and Roving Uniformity*

John P. Elting and James C. Barnes

Kendall Mills Research Laboratories, Paw Creek, North Carolina

Abstract

The addition of a data tabulator to any of the current instruments which graphically depicts sliver, roving, or yarn uniformity vastly extends the usefulness of the instrument. The present paper is intended to provide a working outline. It highlights the nature of the fundamental problems which arise as a consequence of the broad sampling and methods made practical by the tabulator. Illustrations are based on the type of tabulator described by Rusca and applied to the Saco-Lowell sliver tester.

The subjects discussed are: the function of a tabulator, the type of data made available, the minimum continuous sample length, periodicity of variations within a sample, variations between samples, and evaluation of mill machine performance.

THE ADDITION of a data tabulator such as that described by Rusca [9] to any of the familiar graphically recording, irregularity-testing instruments vastly extends the utility of the instrument for both research and mill use. A data tabulator makes practical the rapid accumulation and analysis of sizable quantities of data; broad sampling throughout mill processes may be accomplished. Numerous problems are thereby brought into the foreground, among which are those of experiment design, sampling, and interpretation of results. The present report highlights the nature of these problems as they appear in the light of tabulated data obtained from studies of cotton slivers and rovings with a Saco-Lowell sliver tester. A greater number of practical and theoretical problems involving irregularities of slivers, rovings, and yarn await and deserve attention.

The application of a data tabulator complements and supplements, rather than supplants, the results ordinarily obtained from graphical records. The Kendall tabulator is essentially the same as that described by Rusca, differing principally in that tabulation of the data and the graphical record may be obtained simultaneously. As constructed, the Kendall tabulator does not provide for a variable interval between observations as does the Rusca device. The significance of this latter difference has not been fully appraised; moreover, it is but one of several problems that should be resolved.

The present paper highlights selected steps in the use and interpretation of tabulated data. Much of this material is not new; it is scattered widely throughout the literature and is, in some instances, obscure. This paper is intended as a working outline; the subjects covered are not treated in detail. The references provide information on other and more complete aspects of the uniformity problem.

Automatic tabulation of data as discussed here is not restricted to the Saco-Lowell instrument, and

* Paper presented at the meeting of The Fiber Society, Washington, D. C., September 13, 1950.

it is to be emphasized that problems involving irregularity of mill stocks are so varied that no single testing device, method, or type of data should be expected to yield all the information desired.

What the Tabulator Does

Irregularity may be determined by weighing cut lengths of sliver or roving, but this is, at best, a tedious procedure. Many automatic testing devices have been built which provide a graphical representation of the irregularity of the material examined. The process of taking from these graphs data which are suitable for statistical analysis remains a time-consuming operation.

Possible devices to further reduce the time required for accumulating and calculating uniformity data are numerous and varied. Relatively few such devices have actually been built and described in the literature [1, 2, 4, 9, 15].

The tabulator performs none of the computations. It causes the testing instrument to "observe" at discrete, equally spaced points the thickness of the stock (sliver, roving, etc.) being examined. Counters record the occurrence of these observations. A particular counter shows the number of times that the sliver or roving has a thickness corresponding to that at the moment of observation.

A tabulator effects a major saving of time. It

SACO-LOWELL EVENNESS TESTER

Data: FINISHER DRAWING SLIVER Rack & Pin.: 33 Operator: M.O.P. Date: 6-28-49

Cell Mid-point	-14.5	-13.5	-12.5	-11.5	-10.5	-9.5	-8.5	-7.5	-6.5	-5.5
x	-15	-14	-13	-12	-11	-10	-9	-8	-7	-6
Reading										
Prev. Reading	2348	3601	874	958	1813	721	1032	1893	5219	7362
f										
fx										
fx^2										

Cell Mid-point	- 4.5	- 3.5	- 2.5	- 1.5	- .5	.5	1.5	2.5	3.5	4.5
x	- 5	- 4	- 3	- 2	- 1	0	1	2	3	4
Reading	7277	8735	2040	7351	8262	3013	4654	8052	2453	7596
Prev. Reading	7276	8720	2002	7253	8099	2806	4455	7905	2358	7537
f	1	15	38	98	163	207	199	147	95	59
fx	- 5	-60	-114	-196	-163	0	199	294	285	236
fx^2	25	240	342	392	163	0	199	588	855	944

Cell Mid-point	5.5	6.5	7.5	8.5	9.5	10.5	11.5	12.5	13.5	14.5
x	5	6	7	8	9	10	11	12	13	14
Reading	5384	6860	9557	5219						
Prev. Reading	5367	6857	9553	5217	2404	1665	952	608	443	501
f	17	3	4	2						
fx	85	18	28	16						
fx^2	425	108	196	128						

$\sum f$	$\sum fx$	$\sum fx^2$
1048	623	4605

$$\text{Average: } \bar{X} = \left(\frac{\sum fx}{\sum f}\right) + (\text{Rack \& Pinion}) + 0.5 = \frac{623}{1048} + 33 + 0.5 = 34.09$$

$$\text{Standard Deviation: } \sigma = \sqrt{\left(\frac{\sum fx^2}{\sum f}\right) - \left(\frac{\sum fx}{\sum f}\right)^2}$$

$$= \sqrt{\frac{4605}{1048} - \left(\frac{623}{1048}\right)^2} = 2.01$$

$$\text{Coefficient of Variation: } V = \frac{\sigma}{\bar{X}} \cdot 100 = \frac{2.01}{34.09} \cdot 100 = 6\%$$

FIG. 1. *Sample data sheet for a test run of finisher drawing sliver; the computations and formulas used in computing mean, X, and standard deviation, σ, are shown. Adjustment of the average by an amount equal to the rack-and-pinion setting is necessary with the Saco-Lowell instrument; the 0.5 factor corrects to the cell mid-point. The units used are those established by the Saco-Lowell instrument and correspond to sliver thickness.*

automatically sorts the data and presents it in a form ready for use.

The totals from each counter plotted provide a histogram. The frequency distribution curve is obtained by plotting the percent or fraction that each counter reading is of the total of all counters. Such curves provide a pictorial representation; the shape, breadth, height, and symmetry depict characteristics of the variation. The most generally useful descriptive parameters of the distribution are the mean, $\bar{X}$, and the standard deviation, σ; these are always computed.

The form of analysis and the statistical criteria to be used depend upon how an experiment is designed; the design of the experiment depends upon the information sought. These matters of statistical methodology fall outside the scope of this report. It is pertinent that powerful methods are at one's immediate disposal as a consequence of having adequate data at hand.

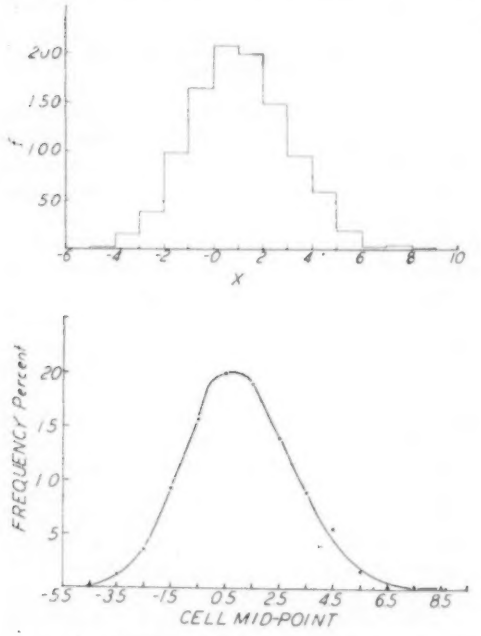


FIG. 2. *Histogram and frequency distribution curves for data given in Figure 1. For the data in the above case, relatively little skewness is indicated.*

The Minimum Continuous Sample Length and Its Subsamples

A single continuous length of sliver or roving may be used to appraise the uniformity of the material in a package. Such a sample must always exceed a certain minimum length.

As continuous samples of increasing length from a single package are tested, the average standard deviation calculated for samples of each length increases and gradually approaches a constant value. The average or mean values for samples of the same length differ among themselves. The standard deviation of these means approaches zero as the length of sample is increased. Graphs for card and second drawing sliver in Figure 3 show that the constant value is approached slowly in the former and rapidly in the latter case. The slow rate of change of standard deviations for card sliver is due to long-term variations which are not recorded until a sufficient length of the sliver has been tested. The rapid change of standard deviations in the case of drawing sliver is due to the absence of long-term variations; the full range is recorded after the passage of a relatively short length of sliver.

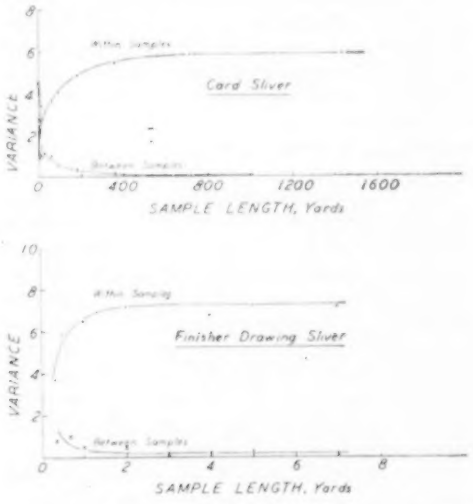


FIG. 3. *Variances (standard deviations squared) within and between samples from a single can each of card and finisher drawing sliver plotted as a function of sample length. As sample length increases, more of the variation is included within each sample; the "between" variances become negligibly small.*

The length of stock beyond which the change of standard deviations may be considered negligible is the minimum continuous sample length. Results from shorter lengths can be very misleading. Longer continuous sample lengths lend assurance that the characterististic values of standard deviation have been approached.

By virtue of this definition, the standard deviation calculated for such a sample is the estimated standard deviation for the specific package whence the sample came. This value is a measure of all irregularities, both short and long, existing within the package. For this reason, the standard deviation based on the minimum continuous sample length or its equivalent is termed the "within" standard deviation.

In the case of the slivers reported here, one may conclude that the minimum continuous sample lengths are approximately 800 yds. and 4 yds. for card and drawing sliver, respectively. Data of Vose and Plummer [15] show that under the conditions of their test minimum continuous sample lengths for card and drawing sliver were approximately 1,300 yds. and 100 yds., respectively. It is reasonable to expect that minimum continuous sample lengths may differ considerably as a consequence of different draft organizations, different equipment, and possibly as the result of different cottons. It is essential, therefore, to determine by preliminary exploration the order of magnitude of the minimum continuous sample lengths which would be appropriate for a particular set of conditions.

Curves such as those shown in Figure 3 yield information other than the length of the minimum continuous sample. If curves for various card slivers are plotted, different rates of change are usually interpreted as indicating the magnitude and extent of variation present in the picker laps from which the slivers were made. The more rapid the change the less likely it is that sliver irregularity may be attributed to that of the picker lap; the causes of short-term variations are to be sought at the card.

Minimum continuous sample lengths are frequently quite long, as in the case of card sliver. It is not always necessary in practice to test the full length of the minimum continuous sample since it in turn may be sampled. The desired result may be obtained by testing subsamples distributed throughout a length of stock at least as long as the minimum continuous sample. Thus, several noncontiguous short pieces of card sliver, each piece being of some convenient length, taken at intervals throughout at least 800 yds. of stock, as in the case illustrated, are an entirely satisfactory equivalent. The aggregate of several subsamples constitutes the test run; the tabulator counters are not read until all subsamples have been observed.

The length of the subsample is of little importance. The total number of observations counted by the tabulator for the entire test run should not be fewer than 30; several hundred are much to be preferred. The number of subsamples, on the other hand, depends upon the information sought. In the usual testing problem where several packages are involved the absolute minimum number is 2; more are desirable. If, however, occasion should arise to determine precisely the characteristics of a specific package, the number of subsamples must be increased and may well be distributed throughout the entire package. In this special case, the number of subsamples should be at least in the range of from 9 to 16, but seldom are more than 30 needed.

Variations Between Samples and Total Variability

If several packages are examined, the average weight or thickness of each will differ to some extent from that of every other. This variation of the averages is also expressed as a standard deviation, in this case between units of stock.

If the several packages constitute a sample from a population, the total variation is the square root of the sum of the squares of the standard deviations within and between packages. This can be written:

$$\sigma_T^2 = \bar{\sigma}_W^2 + \sigma_B^2, \qquad (1)$$

where σ_T is the "total" standard deviation, σ_B is the standard deviation between units; $\bar{\sigma}_W^2$ can in practice usually be either the square of the average or the average of the squares of the "within" standard deviations—the latter is to be preferred. The "total" standard deviation (σ_T) is theoretically a constant for all sample lengths for a particular draft organization and machine settings, etc.

Figure 4 shows plots of the squares of the standard deviations of the "within" and "between" variations for samples of drawing sliver. The "within" variations behave exactly as in the special

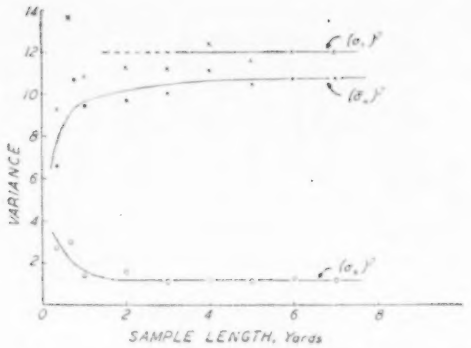


FIG. 4. *Finisher drawing sliver variances plotted as a function of sample length. In contrast with data shown in Figure 3, each of these samples is from a different delivery. The "between" sample variance, σ_B^2, now approaches a constant value which is significantly greater than zero and which is not negligible; this residual indicates the variation between packages. Total variance, σ_T^2, is a constant for the longer sample lengths.*

case discussed for Figure 3. The "between" variations, however, now approach a finite value (greater than zero) as sample length increases. This residual is the "between" variation characteristic of the differences between packages.

Data for the curves of Figure 4 were obtained by use of the sliver tester and tabulator. Savings in time would result, as noted by Townsend [14], by using the sliver tester and tabulator to determine $\bar{\sigma}_W$ for a particular length of sample only. Data for the curve of σ_B^2 *vs.* sample length would then be obtained by weighing samples for each length. By using equation (1), and the assumption that σ_T^2 is a constant, data for the $\bar{\sigma}_W^2$ curve are calculated. This proposal has considerable merit, but it should be noted that additional assumptions are introduced. Values of $\bar{\sigma}_W$ and σ_T so obtained are thus subject to greater error than if the sliver tester and tabulator were used throughout.

The magnitude of the "between" standard deviation for samples equal to or longer than the minimum continuous sample length is a measure of the variation resulting from differences between units of production equipment—*i.e.*, between cards, between draw heads, between spindles, etc.—or between packages from the same unit. A large "between" standard deviation for stock from similar machines connotes a large variation between these elements. This is a concept or interpretation quite different from that associated with the "within" standard deviation.

Although a small total variation is the ultimate goal in textile stock, the relative magnitudes of the "within" and "between" standard deviations are highly significant in determining operating levels and the quality of the product [12, 14]. It may be expected that the process of drafting will increase the "within" whereas doublings will decrease the "between" standard deviations.

Periodicities

In the study of processing equipment, one is occasionally concerned with the short-term variations. These are sometimes obviously periodic, each repeating wave form spanning a specific length of stock that often can be ascribed to some mechanical element of the production machine. For such investigations, only short runs need be made and it is essential to obtain the graphical record. It is through the recorded chart of these short-term variations, not the tabulated data, that periodicities become evident. The tabulated data yield quantitative and useful comparative measures of amplitude, but nothing in regard to frequency. A study of periodicities is valuable in the identification and location of specific machine defects. The interpretation and methods employed in such studies are thoroughly covered by several authors [8, 10, 11].

The tabulator causes the testing instrument to "observe" the stock being examined at equally spaced points along its length. This is a periodic observation. As long as the wave form of the stock is aperiodic or as long as the ratio of the observation interval to the wave length of a periodic variation is irrational, the data compiled by the tabulator are satisfactory. For practical purposes the tabulated data remain entirely acceptable [7]. While the choice of a uniform spacing for the observations admits of theoretical objections, the probability is small that the observation frequency is exactly equal to or is an integral multiple of the wave frequency in the stock. Furthermore, in usual applications of the tabulator, tests are replicated so that observations may be made at different parts of the wave.

Drafting waves have been the subject of a great deal of investigation [3, 5, 6]. They are of concern here because unless the observation interval

is longer than the drafting wave, consecutive observations will not be statistically independent. Even so, this does not appear to guarantee statistical independence except in the case of short-term variations. Longer waves of varying amplitudes are present in most instances (see Figure 5), so that rigorous statistical independence is seldom, if ever, realized. Even though it is true that failure to secure this ideal of independence imposes severe restraints on formal statistical procedures, experience shows that these limitations are of secondary practical importance.

Machine Performance

It is frequently useful to appraise the performance of the machine producing a sliver, roving, or yarn. That the drafting operation always increases the "within" variability of the stock is axiomatic; the uniformity cannot be improved in the absence of some leveling device. For this purpose, minimum continuous sample lengths of stock are required for the test samples.

Vose and Plummer [15] have suggested that the difference between the squares of the coefficients of variation of in- and outgoing stock provides a measure of machine performance. They propose

$$\text{"Damage"} = \sqrt{V_2^2 - V_1^2}, \qquad (2)$$

where V_2 and V_1 are the coefficients of variation of the outgoing and incoming stock, respectively. It is seen that "damage" provides a measure of the variation increment introduced by a machine.

Tippett [13] suggests the use of the ratio of the range of the ingoing stock adjusted for the number of doublings to that observed for the outgoing product. The maximum and minimum values from which these ranges are obtained are those observed in samples of "equivalent" length. This procedure has serious shortcomings, the most serious of which is that the observed ranges, and hence the ratio obtained, depend upon sample length and therefore do not provide a constant characteristic of the machine. An index characteristic of machine performance when minimum continuous sample lengths are used may be obtained in the following manner.

Each individual strand of sliver or roving fed into a machine is characterized by an average thickness, $\bar{X}$, a standard deviation, σ_x, and a coefficient of variation, $V_x = \frac{\sigma_x}{\bar{X}}(100)$. If there are N doublings

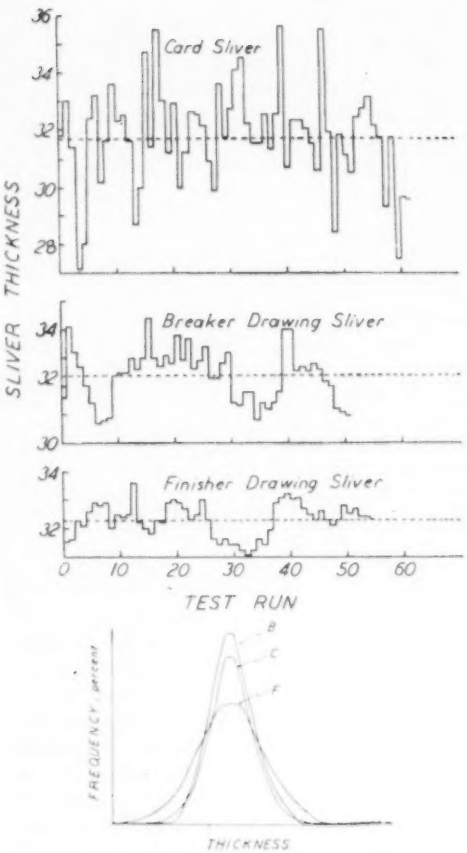


FIG. 5. (a) (top)—*Plots of average thickness for contiguous 30-yd. lengths of card, first drawing, and second drawing sliver throughout a complete package.*

(b) (bottom)—*Plots of the frequency distributions of measurements of thickness made at 1-in. intervals for the 3 cans of sliver shown in* (a). *The curves are superimposed so that the averages coincide; C, B, and F identify card, breaker drawing, and finisher drawing slivers, respectively.*

The reduction in amplitude of the long-term variations shown in (a) *is the result of doublings. The standard deviations of the curves in* (b) *are 2.4, 2.1, and 3.2 for card, first, and second drawing slivers, respectively, which reveals that the total variation increased as the stock progressed through second drawing. Short-term variations not shown must, therefore, have increased in magnitude during this process; the "within" standard deviations based on 30-yd. sample lengths for the above slivers are 1.8, 1.9, and 3.2 for card, first, and second drawing sliver, respectively.*

at the machine, the aggregate input stock is characterized by an average thickness, $N\bar{X}$, a standard deviation, $\sigma_x\sqrt{N}$, and a coefficient of variation,

$$V = \frac{\sigma_x\sqrt{N}}{N\bar{X}}(100) = \frac{\sigma_x}{\bar{X}\sqrt{N}}(100).$$

If the same back stock were fed into a perfect drafting mechanism, having a draft D, the outcoming material would be characterized by an average thickness, $N\bar{X}/D$, a standard deviation, $\sigma_x\sqrt{N}/D$, and a coefficient of variation,

$$V = \frac{\sigma_x}{\bar{X}\sqrt{N}}(100).$$

Noting that $\sigma_x/\bar{X}$ is the coefficient of variation observed for a single strand of ingoing stock, and using subscripts c to designate "calculated for the perfect draft mechanism," o for the observed or measured value, and n to represent a particular process,

$$(V_c)_n = \frac{(V_o)_{n-1}}{\sqrt{N}}$$

would be the coefficient of variation for the nth drafting process if it were a perfect mechanism; $(V_o)_{n-1}$ would be the measured coefficient of variation for the output stock of the immediately prior process. $(V_c)_n$ would be the minimum "within" variation that could result from drafting input stock having a coefficient of variation equal to $(V_o)_{n-1}$.

"Performance ratio," a figure of merit, for the actual drafting machine is given by the ratio of $(V_c)_n$ to the coefficient of variation observed.

Performance ratio thus becomes:

$$(PR)_n = \frac{(V_c)_n}{(V_o)_n} = \frac{(V_o)_{n-1}}{\sqrt{N}(V_o)_n}. \qquad (3)$$

Values of this ratio are always less than unity in the absence of some smoothing mechanism. Values of PR close to unity indicate that the machine is performing almost as well as the imaginary perfect device; small values of PR indicate that the machine is introducing irregularities and that its performance is inferior to one exhibiting higher values.

In applying this formula, coefficients of "within" variation should be used because "between" variations are a function of the number of doublings and not of the draft mechanism.

Literature Cited

1. Anderson, S. L., Cavaney, B., Foster, G. A. R., and Gregory, J., *J. Text. Inst.* **36**, T191 (1945).
2. Anderson, S. L., Cavaney, B., Foster, G. A. R., and Womersley, J. R., *J. Text. Inst.* **36**, T253 (1945).
3. Balls, W. L., "Studies of Quality in Cotton," London, Macmillan, 1928, Chap. 8.
4. Foster, G. A. R., *J. Text. Inst.* **27**, T37 (1936).
5. Foster, G. A. R., *J. Text. Inst.* **36**, T229 (1945).
6. Foster, G. A. R., and Martindale, J. G., *J. Text. Inst.* **37**, T1 (1946).
7. Martindale, J. G., *J. Text. Inst.* **37**, P350 (1946).
8. Plummer, C. H., TEXTILE RESEARCH JOURNAL **15**, 10 (1945).
9. Rusca, R. A., TEXTILE RESEARCH JOURNAL **20**, 780 (1950) (this issue).
10. Saco-Lowell, instruction bulletin: "The Saco-Lowell Graphic Sliver Tester."
11. Steiger, J. U., *J. Text. Inst.* **40**, T253 (1949).
12. Thorndike, G. H., *J. Text. Inst.* **40**, P79 (1949).
13. Tippett, L. H. C., "Proceedings of Ind. Statistics Conference at M.I.T.," New York, Pitman Publishing Corp., 1938, p. 210.
14. Townsend, M. W., *J. Text. Inst.* **40**, P566 (1949).
15. Vose, R. W., and Plummer, C. H., *J. Text. Inst.* **36**, T177 (1945).

(*Manuscript received August 14, 1950.*)

Conversion of the Saco-Lowell Sliver Tester to Electrical Recording*

Ralph A. Rusca

Southern Regional Research Laboratory,† New Orleans, Louisiana

Abstract

The theory and mechanics of converting a Saco-Lowell sliver tester from a graphic-recording instrument to one which records by means of electrical counters are described. General design of the equipment is discussed and photographs of the machine are included. Experience with the converted instrument since March, 1949, indicates that it provides a worth-while improvement in accuracy and in speed of analyzing the uniformity of sliver and heavy roving.

RECENTLY, progressive cotton textile management as well as mill personnel have been aware more than ever of the importance of quality control in mill operations. Possibly this greater emphasis on quality control is due in part to the influence of World War II, which has caused more widespread buying of textile products on customer specifications. One manifestation of the increased interest has been the demand by industry and research for the development of more rapid methods for measuring sliver and roving uniformity as a means of improving the quality of cotton yarns.

Equipment

Numerous methods of effecting savings of time and making possible the rapid evaluation of uniformity of slivers and rovings have been described and discussed in the literature. Mechanical [4, 5], electrical [3, 7], photographic [1, 2], photoelectric [6], thermal [8], and other methods have been reported. An example is the application to a Saco-Lowell tester of an electric integrating circuit devised by Vose and Plummer [7]. The instrument uses watt-hour meters to integrate the variations in thickness; average and standard deviations are obtained immediately from the readings shown on the meters. All of the devices described in the literature are complex, in varying degree, and only a few are readily adaptable to the Saco-Lowell instrument.

The present paper describes an instrument which replaces the usual recording chart by a series of electrical contacts over which the recording arm passes in accordance with the thickness of the sliver. Credit for the original design or concept for this is believed to be due to the Research Laboratories of Kendall Mills; the instrument was described at a meeting of The Fiber Society, Charlotte, N. C., September, 1943. The tabulator described in this paper and the Kendall tabulator [3] embody several distinct improvements and features. It is felt that this tabulator system provides about the simplest and least expensive method of securing and organizing large quantities of good statistical data. The combination of the tabulator and the commonly used Saco-Lowell instrument would therefore provide a powerful analytical tool, easily within the reach of mills and laboratories throughout the country.

The Saco-Lowell sliver tester probably is the instrument most used for determining the uniformity of sliver and 1.5-hank and heavier roving. It is an instrument designed to measure the cross-sectional uniformity of a continuous length of material, and to provide a permanent record of the data by means of a conventional strip-chart recording mechanism. A Saco-Lowell tester has been modified at the Southern Regional Research Laboratory, and since the converted tester has proved very useful in the Labora-

* Paper presented at the meeting of The Fiber Society, Washington, D. C., September 13, 1950.

The mention of trade products does not imply their endorsement by the Department of Agriculture over similar products not mentioned.

† One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

tory's textile research work, its general construction will be described with the idea that it may aid in the search for improved methods of evaluating sliver and heavy roving.

The Southern Laboratory's instrument has a fully electrical tabulating system, a method for varying the incremental length of sliver or roving measured, and a separate method for measuring a constant increment for reference purposes. Other useful features are an automatic electrical knock-off motion and A.C. voltage stabilization.

The Saco-Lowell tester is a comparatively simple device that subjects sliver to a predetermined pressure and measures the thickness of the compressed sliver in terms of .001 in. In operation, the sliver is passed between a grooved bottom roll and a resting top roll at a fixed speed of 1 yd. per min. The top roll is said to exert about 1,600 p.s.i. on sliver and 2,500 p.s.i. on roving by means of a compound lever system and weights. Movement of the top roll in response to variations in uniformity (compressibility) actuates an arm on which is mounted a capillary pen. The pen in turn marks a strip chart that has a linear motion of 1 in. per in. of sliver or of 3 in. per yd. of sliver. This chart is graduated vertically in thirty .1-in. increments, marked ± 1 to ± 15 from a common center line. It is customary to test 30 in. of sliver at the slow chart speed and 20 yds. of sliver at the fast chart speed.

Theory

Converting the Saco-Lowell sliver tester consists essentially of substituting electrical counters for the graphic-recording system. Certain theoretical considerations were the starting point of the adaptation. The basic part of the electrical conversion is a commutator system that replaces the strip chart. Let it be assumed that the thirty .1-in. chart spaces are replaced with 30 insulated bars of copper, and that each bar is connected to its individual electromagnetic counter. Assume further that the conventional capillary pen is replaced with a suitable contactor point. If these parts can be arranged in an electrical circuit in such a manner that the contactor will be powered at predetermined intervals, that particular counter which is connected to the copper bar on which the contactor rests will be energized as long as the contactor remains on the bar, or until the circuit is broken by external means. Let this external means be a timing device which controls the frequency of making the circuit and the length of time the circuit is allowed to remain energized.

In the operation of a system of this description, as the sliver passes through the tester the contactor point would move up and down the copper bars in accordance with the uniformity of the sliver. When the timer completes the electrical circuit the counter connected to that copper bar on which the pointer was contacting at the moment would register. If, for example, the sliver was moving at 1 yd. per min. and the timer was set to make and break the circuit 30 times a min., the sliver would be measured in 1-in. increments.

Mechanical Considerations

Construction of such an apparatus is made difficult by a number of practical mechanical considerations. Firstly, the insulating material between the commutator bars must be adequate to prevent electrical flashover and must also be thick enough to prevent the bridging of two bars by the contactor point. On the other hand, the thickness of the insulator governs to a large extent the sampling response of the apparatus. Should the bars and the insulators be of the same thickness, theoretically one-half of the points would not be measured because the circuit would be completed one-half of the time with the contactor on an insulator. Using thin insulators and an extremely pointed or a wedge-shaped contactor would increase sampling response, but the general wearing qualities of these parts would be seriously impaired.

To further complicate construction, the timing interval must be a compromise between a very short time to allow the moving contactor to energize only one counter and a longer time to give the required amount of electrical energy for the electromechanical counter.

The ideal counter for this application was found to be a unit of small dimensions with an electrical reset. Commercially available counters generally are of three types: (1) small, non-resettable, low voltage D.C., telephone type, costing about $12; (2) large, heavy, electrically resettable, 110 volts A.C. or D.C., costing about $35; (3) small, non-resettable, 110 volts A.C., costing about $6. Although it is highly desirable to use the resettable type of unit and thereby avoid the possibility of operator errors in copying and subtracting 30 sets of multidigit figures, the last-named counter was selected for the SRRL machine on the basis of size and cost.

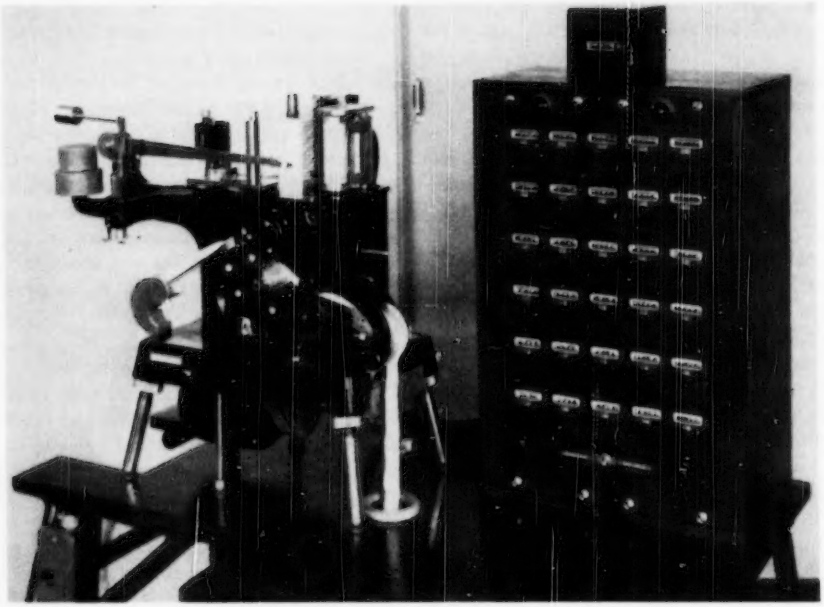


FIG. 1. *Converted sliver tester, showing general layout of the counters and associate equipment.*

Construction

Figure 1 gives an idea of the general layout of the parts. The counters and signal lights, with their associated relays and switches, are inside a 6-in.-deep box behind a 12¼ in. by 19 in. standard relay rack steel panel. On top of the sliver tester can be seen the parts that have replaced the conventional chart-recording mechanism.

Figure 2 shows the top of the tester. The contactor point, commutator, adjustable eccentric, yardage counter, and the 33-wire cable (30 counters, 1 common ground, 2 A.C. line) going to the control box are seen.

A rear view of the apparatus (Figure 3) shows the wiring layout of the counters and the external variable-speed timing device. The fixed reference timer is built-in under the sliver tester proper, and is concealed by the sheet-metal guard adjacent to the left leg. Rubber casters facilitate movement of the equipment around the mill.

The construction and mounting of the miscellaneous mechanical parts is an uncomplicated job. Little change is necessary in the original sliver tester except to remove the chart, chart plate, and windup table, and to cut down the size of the top plate holding the knurled-friction roll-chart drive.

Referring again to Figure 2, a machined steel plate is fitted on top of the tester to provide a flat surface for mounting the commutator bars and eccentric. The latter parts are fastened to individual steel plates, which in turn are screwed to the first large plate. By this means, the bars and eccentric can be more accurately located parallel to each other and to the contactor point. The contactor point is adjusted along its horizontal axis until the contactor describes the proper arc on a flat surface on the commutator bars. The error introduced by the arc of the pen arm causing the contactor to traverse a longer path on bars ±15 than on bars ±1 has been found to be negligible. It should be noted that the length of the pen arm is designed for the dimensions of a specific commutator assembly; in this particular installation it is 10¾ in. Should thicker bars or insulators be utilized the pen arm would be longer, and vice versa for thinner ones.

An eccentric rod regulates contact pressure on the copper bars, while a small piece of sponge rubber

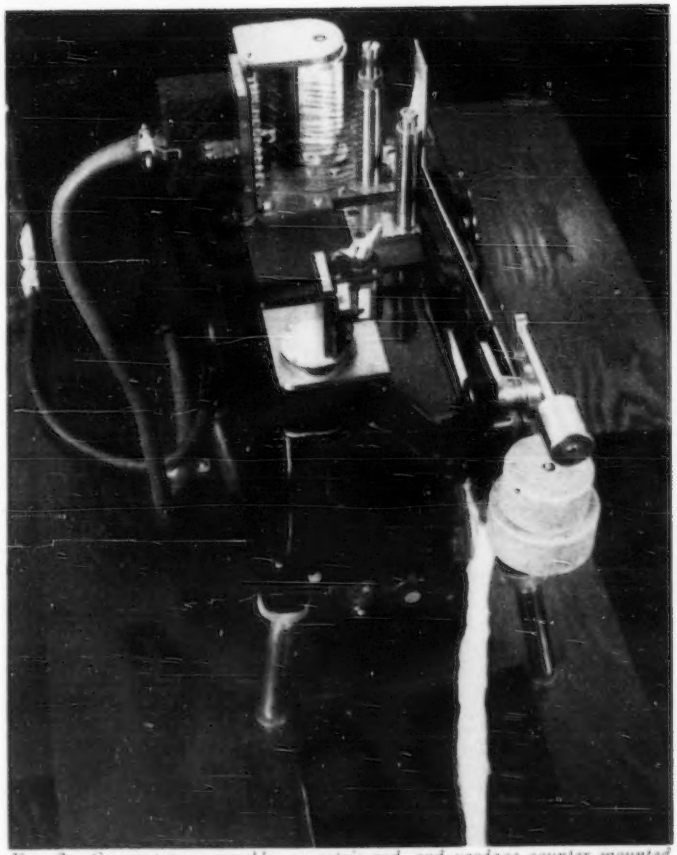


FIG. 2. *Commutator assembly, eccentric rod, and yardage counter mounted on top of the converted sliver tester.*

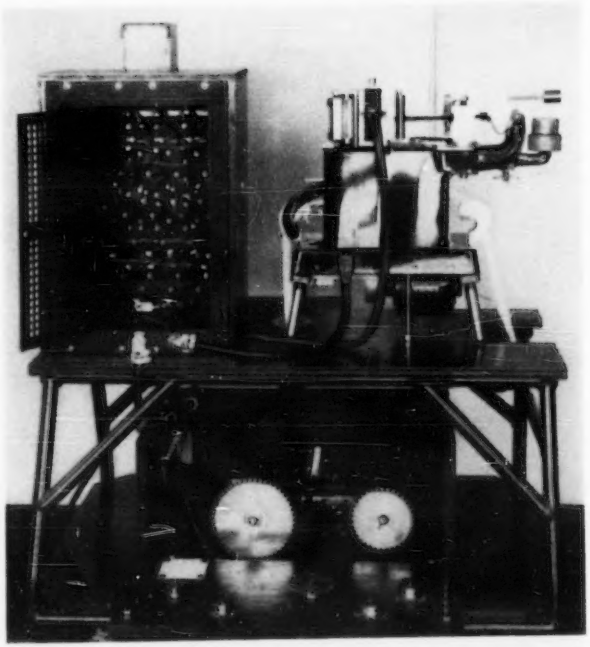


FIG. 3. *View of the rear of the converted sliver tester, showing the interior of the counter control box and the external variable-speed timer.*

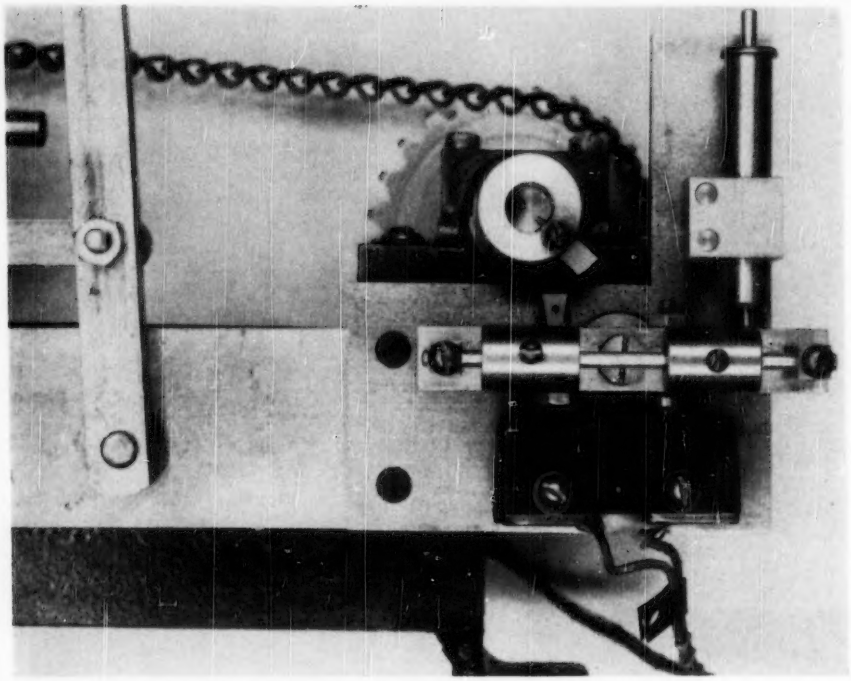


FIG. 4. *External timer with spring-actuated switch.*

placed back of the contactor point allows a small in- and out-movement of the point and makes the eccentric adjustment less critical. A discarded ball-point fountain pen has proved very satisfactory for the contactor point.

The reference timing cam, which measures each 2.3 in. of sliver, is driven by a pair of spur gears added to the sliver tester. The cam is designed to close a sensitive snap-switch for .05 sec.

Considerable difficulty was encountered with timing the external variable cam to permit measuring sliver over the wide range of ½-, 1-, 2-, 3-, 4-, 6-, 12-, and 18-in. lengths. Since the desired timing interval of .05 sec. could not be obtained by allowing the cam to strike directly on the snap-switch plunger, a mechanism was devised whereby the cam strikes a balanced pivot bar, which in turn compresses a coil spring, and the spring releases to snap the switch with the same degree of force regardless of the rotational speed of the cam. Figure 4 shows the general appearance of this device.

A simplified block diagram of the apparatus is presented in Figure 5; a schematic diagram of the electrical circuit is given in Figure 6.

The use of non-resettable counters is facilitated by one other modification of the tester. The clutch that normally shifts the chart speed is modified to trip a

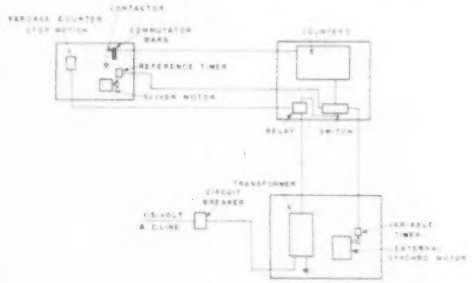


FIG. 5. *Simplified block diagram of the converted sliver tester.*

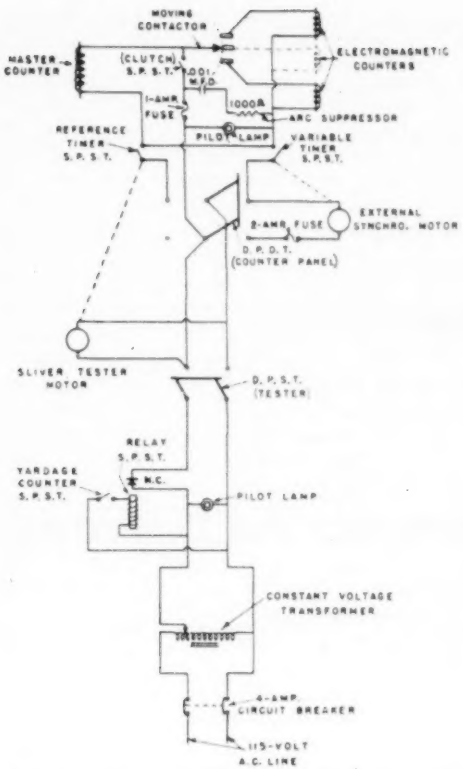


FIG. 6. *Schematic diagram of the electrical circuit.*

snap-switch so that the counters will not register until the clutch lever is thrown to the proper position. Disengaging the clutch disconnects the counters and makes it possible to change the sliver or to make a machine adjustment without disturbing the counters, the main advantage being that the last set of figures copied from the counters at the completion of a test will also serve as the first set of figures for a new test, thereby decreasing the possibilities of operator error.

The knock-off motion is devised from a rotary digit counter and a small snap-switch. The counter, which is installed on the chart windup table, is driven through suitable gearing to register in tenths of a yard. At the completion of 20 yds. the switch disconnects the electric power and stops the machine, thereby permitting the machine to operate unattended for the 20-min. test interval.

Results

Experience with the converted sliver tester at the Southern Regional Research Laboratory since March, 1949, has shown that a skilled calculating-machine operator can copy the totals from the counters and compute the mean, standard deviation, and coefficient of variation of sliver uniformity in about two-thirds of the time required for measuring the points on a strip chart and making similar statistical computations. Using resettable counters would further decrease operator time for this method. The time required for running the sliver through the converted tester or the conventional tester, however, is the same.

A major advantage of electrical recording is the larger number of sample points available for statistical treatment. The standard chart system uses 30 points in 30 in. of sliver from which to compute the "average variation per inch," and 20 pairs of high-low points in 20 yds. of sliver to compute the "average maximum variation per yard." With electrical recording, up to 1,440 points can be used for determining the uniformity, including the mean thickness, average variation from the mean, standard deviation from the mean, and coefficient of variation of the sliver or roving. Moreover, the variable of operator judgment in measuring a graphic record is eliminated.

Conclusion

The converted sliver tester used at the Southern Regional Research Laboratory for more than $\frac{1}{2}$ year on textile research applications has proved to be a worth-while development. It is believed that an instrument of this type would be valuable in the field of textile production, and that this general technique of electrical recording might be applied advantageously to other testing instruments which provide data requiring standard statistical treatment.

Acknowledgment

The author wishes to express appreciation to Mr. John P. Elting and associates of Kendall Mills for discussing their instrument, and to Mr. Herbert R. Copeland, Instrument Maker of the Southern Regional Research Laboratory staff, for his skillful conversion of the sliver tester.

Literature Cited

1. Anderson, S. L., Cavaney, B., Foster, G. A. R., and Gregory, J., *J. Text. Inst.* **36**, T191 (1945).

2. Anderson, S. L., Cavaney, B., Foster, G. A. R., and Womersley, J. R., *J. Text. Inst.* **36**, T253 (1945).
3. Elting, J. P., and Barnes, J. C., TEXTILE RESEARCH JOURNAL **20**, 773 (1950) (this issue).
4. Johannsen, O., *Kleipzigs Textil-Z.* **41**, 369 (1938).
5. Saxl, I. J., *J. Text. Inst.* **26**, T77 (1935).
6. Stanbury, G. R., *J. Text. Inst.* **22**, T385 (1931).
7. Vose, R. W., and Plummer, C. H., *J. Text. Inst.* **36**, T177 (1945).
8. Whitehead, W. and J., Ltd., Steward, O. M., and Smith, E. P., B. P. 343,215 (Dec. 4, 1929).

(Manuscript received August 31, 1950.)

"Orlon" Acrylic Fiber: Chemistry and Properties*

R. C. Houtz

Pioneering Research Section, Rayon Technical Division, E. I. du Pont de Nemours and Company, Wilmington, Delaware

AFTER EXTENSIVE RESEARCH and development on fibers from polyacrylonitrile, the du Pont Company in 1948 announced its intention to produce and market a line of fiber products based upon this material. The trademark "ORLON" was adopted to designate du Pont fibers produced wholly or in substantial part from acrylonitrile. Manufacture will be carried out at a plant now under construction at Camden, South Carolina.† It is expected that production will be initiated during the latter part of 1950.

Orlon acrylic fiber will thus take its place as a new member of a small but increasingly important group of fibers of truly synthetic origin. This group already includes nylon and several fibers based on vinyl halide derivatives.

The polymerization products of acrylonitrile have long been known. They have been notable as compared to other vinyl polymers for their insolubility and resistance to swelling in common organic solvents. This fact, perhaps more than any other, prevented their early exploitation in such fields as plastics or synthetic textiles. In one school of thought this insolubility was attributed to a cross-linked structure. In others this property was associated with strong, secondary interchain forces. The work of Marvel [3, 11] and coworkers on the relation of hydrogen-bonding forces in polymers to solubility in polar monomeric solvents tended to support the latter view.

Stimulated by the concepts of Marvel, our initial work was directed toward the finding of highly polar organic molecules which might be sufficiently strong in hydrogen bonding to break up the interchain forces which are presumed to exist within the polymer itself. The early years of our work were devoted to a broad, fundamental program relating to the solvent power of organic materials for polyacrylonitrile in an attempt to establish the underlying principles of solubility. As a result, a large number of solvents [22–36] have been discovered in our laboratories; these

* This paper is a condensation of an address given by the author before the Gordon Textile Conference at Colby Junior College, New London, New Hampshire, July 18, 1949.

† Since this paper was submitted for publication, commercial production of Orlon acrylic fiber at Camden, S. C., has been begun.

represent several classes of organic compounds. These solvents have made possible the manufacture of polyacrylonitrile fibers.

Concurrently, work was also devoted to the practical problems related to the spinning of textile fibers from many of the various polymer solutions at hand. This latter work had progressed to the point where in 1942 experimental samples of the new fiber products were offered provisionally for certain classified military applications. This work expanded and progressed actively during the war on the basis of military uses. However, after the cessation of hostilities, the more conventional textile uses for the fibers began to receive increasing attention, with still further broadening of our development activities, which culminated in a decision on the part of the Company to enter into the large-scale manufacture referred to above.

Subsequent to the end of the war, Rein [16, 17] disclosed that the I. G. Farbenindustrie had also been active in the field of solvents for polyacrylonitrile, as well as in that of fibers produced thereby. Many of the same solvents which were discovered in our laboratories and later disclosed in U. S. patents were also the subject of German patent applications which had been filed but kept secret during the war. However, these documents do not indicate a recognition of the severe structural limitations on solvent compounds which are discussed in the present paper. Many compounds which are certainly nonsolvents had been disclosed in the German patents as solvents.

Our early work, as pointed out above, was concerned with the search for inert, polar, organic solvents which would dissolve polyacrylonitrile. Predictions based upon the probable structure of this polymer, together with its known high melting point, likewise stimulated this search. The success of this study of solvents has more than satisfied our early expectations, because not only were the expected fiber properties realized but also many new, unexpected, and important fiber properties were later found which could not have been predicted from our earlier background work on polymers. These have been brought to light gradually throughout the course of a long and intensive research program.

This paper deals with solvents, with the chemistry of polyacrylonitriles, and with certain chemical and physical properties of fibers prepared from them. Work on such subjects as polymerization of acrylonitrile and fields of application for Orlon acrylic fiber has been reported elsewhere [10, 15] and is not discussed here. Since the articles referred to also contain much information on the physical properties and the durability characteristics of Orlon, only a condensed discussion of these is presented here.

Solvents

As might have been expected from the fact that polyacrylonitrile was long considered to be completely insoluble, none of the more common types of solvents which are normally used for polymers, such as hydrocarbons, alcohols, esters, ethers, and ketones, were found to be effective. However, during the course of solubility testing, in which several thousand organic compounds and mixtures were tried, a fairly large number of compounds bearing specific functional groups were found to have solvent action. The solutions once formed exhibited characteristics common to those of other polymer solutions. They tended to show unlimited solubility; the solutions were viscous; and many of the solutions gelled reversibly on cooling, so that fluid solutions were reobtained on heating. From these solutions, fibers, films, and other-shaped articles could be formed by the well-known means of evaporating off solvents, or by coagulating the polymer in suitable liquid media. In Table I are listed a few representatives of several of the classes of solvents investigated during the course of this work. Listed also are several closely related nonsolvents which illustrate the limiting structural factors involved.

Dimethylsulfone and ethylmethylsulfone are good solvents, whereas the compound with one more methylene group, diethylsulfone, only swells the polymer. It is evident from this comparison, as well as from numerous others, that the active or "solvogenic" group can be combined in the solvent molecule with a certain amount of inactive material, such as hydrocarbon residues, but that when this amount is exceeded solvent power is lost. This tolerance is greater in ring compounds than in straight-chain compounds. In the ring compound sulfolane the tolerance for methylene groups is higher than it is in the open-chain compounds. However, this limit is soon exceeded, because if two methyl groups are substituted on the ring a nonsolvent results. If more than one solvogenic group is present in the molecule, a larger number of carbon atoms can be tolerated before solvent power is lost. This is illustrated by ethylene 1,2-bis(ethylsulfone); however, in sulfonal

TABLE I [22–36]. SOLVENTS AND RELATED NONSOLVENTS FOR POLYACRYLONITRILE

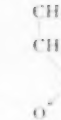
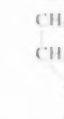
Solvents		Related nonsolvents	
Dimethylsulfone		Diethylsulfone	(swells)
Ethylmethylsulfone		Diallylsulfone	
Sulfolane		3,4-Dimethylsulfolane	
Ethylene 1,2-bis(ethylsulfone)		Sulfonal	
2-Hydroxyethylmethylsulfone		bis(2-Hydroxyethyl)sulfoxide	
Dimethylsulfoxide		Diethylsulfoxide	(swells)
Tetramethylenesulfoxide		*n*-Butylmethylsulfoxide	
Dimethylformamide		Formamide	
		Diethylformamide	
		Methylformamide	
Dimethylthioformamide			
Tetramethyloxamide		Dimethyloxamide	
		Tetramethylurea	
Dimethylmethoxyacetamide		*N*-Methyldiacetamide	
		Methoxyacetamide	

TABLE I—*Continued*

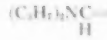
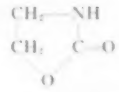
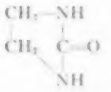
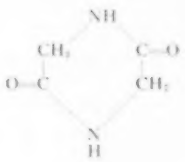
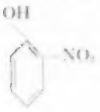
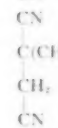
Solvents		Related nonsolvents	
N-Formylhexamethyleneimine		Dipropylformamide	
2-Oxazolidone		Ethyleneurea	
N,*N*′-Diformylpiperazine		Diketopiperazine	
ε-Caprolactam		*N*-Butylformamide	
Phenylenediamine (*o*, *m*, and *p*)	$C_6H_4(NH_2)_2$	1,6-Hexanediamine	$H_2N(CH_2)_6NH_2$
Nitrophenol (*m* and *p*)		*o*-Nitrophenol	
Succinonitrile		Acetonitrile	CH_3CN (swells)
Malononitrile		Methylmalononitrile	
		Dimethylmalononitrile	
		α,α-Dimethylsuccinonitrile	
Adiponitrile		Suberonitrile	

TABLE I—*Continued*

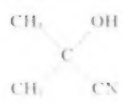
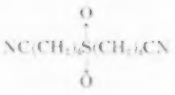
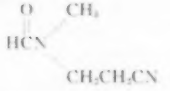
Solvents		Related nonsolvents	
bis(β-Cyanoethyl)ether			
bis(β-Cyanoethyl)sulfide			
Fumaronitrile			
Hydroxyacetonitrile	$HOCH_2CN$	Methoxyacetonitrile	CH_3OCH_2CN
β-Hydroxypropionitrile	$HOCH_2CH_2CN$	β-Methoxypropionitrile	$CH_3OCH_2CH_2CN$
		α-Hydroxypropionitrile	CH_3CHCN (swells)
		α-Hydroxyisobutyronitrile	
1,3,3,5-Tetracyanopentane			
Methylenedithiocyanate		Methylthiocyanate	
Trimethylenedithiocyanate		Hexamethylenedithiocyanate	
α-Cyanoacetamide			
γ-Butyrolactone		Propylformate	

TABLE I—*Continued*

Solvents		Related nonsolvents
bis(4-Cyanobutyl)sulfone		
N-Methyl-*β*-cyanoethylformamide		

the effective ratio has been exceeded and the compound is a nonsolvent. Substitution of a hydroxyl group for a hydrogen atom can be tolerated. In general, sulfoxides behave similarly to sulfones, as illustrated again by dimethylsulfoxide and the nonsolvent diethylsulfoxide. The hydroxyl group does not appear to affect the carbon tolerance, since in bis(2-hydroxyethyl) sulfoxide solvent action has again been lost. As with sulfones, carbon tolerance is greater in the sulfoxides containing rings, exemplified by tetramethylenesulfoxide.

The same principles of carbon tolerance and of ring compounds apply to the group of formylamines. Dimethylformamide is a solvent; diethylformamide is not. The need for complete substitution of the amide hydrogens is illustrated by formamide and also by methylformamide, which are nonsolvents. That sulfur can be substituted for oxygen is exemplified by dimethylthioformamide.

It is seen that nitriles of certain structures are also solvents. Acetonitrile exerts a swelling action only at very high temperatures. The short-chain aliphatic dinitriles, however, are solvents—*e.g.*, malononitrile, succinonitrile, and adiponitrile. In suberonitrile the limit of carbon tolerance is exceeded and solvent action is again lost. There is reason to believe that the active solvogenic group in this series is the —CHCN group. For example, methylmalononitrile and dimethylmalononitrile are not solvents, while succinonitrile and glutaronitrile are. A solvent containing four nitrile groups, including —CHCN groups, is illustrated by 1,3,3,5-tetracyanopentane. Other nitrile-type solvents have been found in compounds with oxygen or sulfur substituted in the chain—for example, bis(*β*-cyanoethyl) ether and bis(*β*-cyanoethyl) sulfide. Again, the introduction of unsaturation (the C=C double bond), as in fumaronitrile, has little effect. However, in conjunction with the nitrile group, the hydroxyl group has solvogenic activity, as illustrated by hydroxyacetonitrile. The methoxy group in this case is not effective, as shown by methoxyacetonitrile, a nonsolvent. The hydroxyl group is also effective on the *β*-carbon, as in *β*-hydroxypropionitrile. Again, etherification destroys the solvent power. Other structural effects are illustrated by the fact that α-hydroxypropionitrile (lactonitrile) only swells, and by the nonsolvent α-hydroxyisobutyronitrile.

Thiocyanates behave somewhat similarly to the nitriles. The first member, methylthiocyanate, is ineffective, but the addition of the second thiocyano group, as in methylenedithiocyanate, produces a solvent. Carbon tolerance limits here are illustrated by trimethylenedithiocyanate, a solvent; higher members of the series are ineffective.

The unsubstituted amide group, although usually ineffective, becomes solvogenic in character in combination with the nitrile group, as indicated by cyanoacetamide. Many other combinations of these groups are possible. Two further illustrations of such a combination are the compounds bis(4-cyanobutyl) sulfone and *N*-methyl-*β*-cyanoethylformamide.

In certain cyclic oxygen-containing compounds, such as γ-butyrolactone, the same principles apply.

The nonsolvent effect of *o*-nitrophenol, in contrast to the solvent effect of *m*- and *p*-nitrophenol, probably relates to the bimolecular chelate ring formation in the former [1], rendering it less able to bond with polyacrylonitrile.

H. Rein [37, 38] claimed that concentrated aqueous solutions of certain inorganic salts, such as lithium bromide, would dissolve polyacrylonitrile. These, however, were found not to be useful, because polyacrylonitrile could not be recovered from

them. Instead, chemical reactions occurred, which were accompanied by marked changes in properties.

Theories of Solvent Action on Polymers

Naturally, it would be desirable to have a complete theory to explain and predict effects of solvents on polyacrylonitrile and, indeed, on all other polymers. No such theory has yet been devised, although various attempts have been made in the past 10 years to place the solubility of polymers on a sound scientific basis. These attempts range from qualitative descriptions of similarity in structure to theoretical thermodynamic approaches based on certain physical constants and on quantities derived from them. The latter have been ably summarized in a paper by Spurlin [21]. It has long been known that similarities in the composition and structure of molecules tend to render them mutually soluble; for example, unvulcanized rubber is soluble in hydrocarbon solvents. We have seen above that polyacrylonitrile is soluble in di- and polynitriles, but not in monomeric acrylonitrile. Coltof [2] has made a large number of solubility tests on such polymers as cellulose acetate and polyvinylchloride; he describes the solvents in terms of specific effects of certain groups within the solvent molecules. As noted above, solvents for polyacrylonitrile can also be described in terms of the effects of specific groups. After a considerable number of solvents have been found for a given polymer, such classifications are useful in predicting other solvents. These classifications fall short of explaining solvent behavior.

From the theoretical side, G. Gee and several others have advanced the concept of internal pressure or cohesive energy density to explain solubility. Qualitatively, this may be described as the tendency of molecules to separate from each other. Solubility is usually found where this tendency for both the solvent and the solute are nearly equal. This theory has had its principal success in explaining solution of nonpolar polymers, such as rubber, rather than that of polar or crystalline polymers, since it neglects such factors as solvation, crystallinity, and entropy of solution. Flory [4, 5] and Huggins [7] have developed relationships between the activity of polymeric solutes and their solvents for dilute polymer solutions, which purport to take these latter factors into consideration. The factor μ, which is a measure of the deviation of the solution from ideality as expressed by Raoult's law and which can be determined, for example, by the slope of the osmotic pressure-concentration curve, contains both an entropy and an energy term. A few values of μ have been determined for several good polyacrylonitrile solvents and have been found to be in the range required by the Flory-Huggins theory.

This and other theories, in order to be generally applied for prediction of solvent effect, require first the determination of the needed experimental quantities *on the polymer solution*. This, of course, presupposes having the solution in hand. From a very large number of such data one would then need to calculate and predict μ values for other solutions which have not yet been made. There seems at present to be no theoretical basis for calculating, for example, μ values for an untried solution from data obtained on a given known solution.

Another qualitative approach to the explanation of solvent action on certain polar-type polymers can be made through the concept of hydrogen bonding. This concept was first applied to the solubility of low-molecular-weight compounds in each other by Marvel [3, 11] and coworkers, who studied hydrogen-bonding capacity both by means of measurements of the deviation from Raoult's law of the solubility of gases in liquids and by heat-of-mixing measurements. This has been a useful concept in seeking new solvents for polyacrylonitrile. As will be indicated later, the high-melting nature of the polymer can be ascribed to hydrogen bonds existing between the α-hydrogen and the nitrile nitrogen of an adjacent chain. It is presumably this bond, therefore, that must be broken in order to form a solution. Ideally, then, we should choose a solvent molecule which has a tendency to bond at these two points more strongly than two or more solvent molecules tend to bond together. From the published work on hydrogen bonding, plus an examination of the formulas for the solvents described above, it will be seen that most of them contain both donor and acceptor centers. For example, the nitrile group would be the donor group, and the α-hydrogen of the di- and polynitriles the acceptor. Sulfone groups are known to be electron donors, and the α-hydrogens are probably the acceptors. Far too little is known about hydrogen-bond distances and strengths in the variety of combinations of molecular groupings to permit the forging of this concept into a complete theory of solvent effects in polar-type polymers.

Probably all of the principals which have been discussed above apply to some degree, and with the acquisition of a very large amount of data of the type indicated a theory of solvent action which would be generally useful in the prediction of solubility behavior should eventually emerge. Meanwhile, far more rapid progress toward finding useful solvents can be made by direct solubility testing, employing any empirical rules which seem to apply.

Fractionation and Molecular-Weight Determination [9]

The differences in solubility between polyacrylonitrile samples of various molecular weights are small, and this has rendered difficult its separation into fractions of narrow molecular-weight range. However, fractionation of polyacrylonitrile has been successfully carried out using mixtures of dimethylformamide and heptane. A 2% solution of the polymer in dimethylformamide was treated with the requisite amount of heptane at room temperature. The temperature was then raised to 60°C, whereupon the hydrocarbon layer disappeared and a portion of the polymer precipitated out in granular form. After carrying out a rough fractionation, the procedure was repeated on a 1% solution of the polymer. Data for a typical fractionation are given in Table II. The intrinsic viscosities were determined in dimethylformamide solution. Fractionation was not accurate enough for a precise determination of molecular-weight distribution, but from these and similar data it would appear that the distribution follows the normal distribution curve, with some skewness toward the high-molecular-weight end.

TABLE II. FRACTIONATION OF POLYACRYLONITRILE (15 G. POLYMER, 1% SOLUTION)

Fraction	% Heptane in dimethylformamide	Wt. of fraction (g.)	$[\eta]$
1	22.3	0.9907	4.35
2	22.5	4.9736	4.58
3	22.8	.7808	4.54
4	23.4	2.3871	3.78
5	24.2	1.0332	2.84
6	25.0	1.5298	2.27
7	25.7	.8891	1.70
8	28.0	.7295	1.07
9	30.5	.4732	.98
10	—	1.2836	.93
		Total 15.0706	

TABLE III. RELATION OF INTRINSIC VISCOSITY TO MOLECULAR WEIGHT FOR POLYACRYLONITRILE FRACTIONS

Fraction	$[\eta]^*$	M
1	4.048	135,000
2	3.911	113,000
3	3.673	131,000
4	3.124	77,000
5	2.788	66,000
6	2.696	62,000
7	2.382	69,000
8	1.65	44,000
9	1.111	17,600

* $[\eta] = 1.75 \times 10^{-3} M^{0.66}$.

Fractions obtained in this way were subjected to osmometric determinations of number-average molecular weight. All-glass osmometers of the type described by Schultz [20] were used. Molecular weights were calculated from the slopes of the plots of π/C vs. C, where π is osmotic pressure and C is concentration. Representative molecular-weight data appear in Table III. From the determination of molecular weight on each fraction listed in the table the constants a and K in the equation

$$[\eta] = KM^a,$$

where $[\eta]$ is intrinsic viscosity and M is molecular weight, were calculated and found to average 0.66 and 1.75×10^{-3}, respectively. The molecular weight-intrinsic viscosity relationship was thus found to be

$$[\eta] = 1.75 \times 10^{-3} M^{0.66}.$$

Number-average molecular weights have been measured on whole polymers prepared in various ways, and, using several of these, the ratio of viscosity-average to number-average molecular weight has been found to be approximately 2. This is another indication of approximately normal molecular-weight distribution, since on the theoretical curve the ratio is exactly 2.

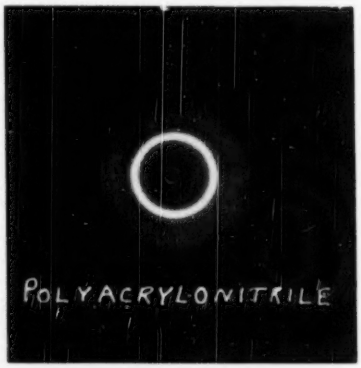
Chemical Structure

Marvel [12] and coworkers have shown by means of chemical-degradation experiments on a number of vinyl polymers that the normal mode of addition is head-to-tail. That there are some exceptions to this rule was recently demonstrated by Flory and Leutner [6], who studied the structure of polyvinyl alcohol by means of periodate oxidation experiments. They showed that although the molecule has principally the structure of a head-to-tail-addition polymer some

head-to-head linkages occur. Kern and Fernow [8] speculated on the possibility of head-to-tail structures *vs.* other possible structures for polyacrylonitrile, including that of cross-linking, to account for its then supposed insolubility. They considered the head-to-tail structure to be the most probable, with the insolubility of the polymer resulting from strong interchain forces between the nitrile groups.

Polymethyl acrylate and polymethyl methacrylate are considered to be normal head-to-tail-addition polymers. Certain analogies with their nitrile counterparts exist in the behavior of these two polymers on saponification and on pyrolysis. The methacrylate and methacrylonitrile polymers are both extremely difficult to saponify, and they depolymerize principally to monomer on heating. The acrylate and acrylonitrile polymers, on the other hand, are relatively easily saponified by hot aqueous alkali, and they decompose on heating not to monomers but to a variety of low-molecular-weight cleavage products. Pyrolysis of polyacrylonitrile at 400°C has given small amounts of low-molecular-weight amines (but little or no HCN), which have not been further identified.

Some evidence bearing on structure has been obtained by means of x-ray and infrared studies on polyacrylonitrile. The x-ray diffraction diagram of the polymer indicates that it is unoriented and partially crystalline (Figure 1). The diffraction diagram of the drawn fiber is, on the other hand, highly oriented and indicates the complicated type of order which characterizes this material. The most striking feature is the diffuseness of the off-equatorial reflections, which is indicative of disorder along the chain axis. The comparative sharpness of the two prominent equatorial reflections (one of which is the second order of the other) is a manifestation of the high degree of order in one lateral direction. The spacing, 5.3 A., is associated with the distance between polymer chains through the nitrile group—that is,



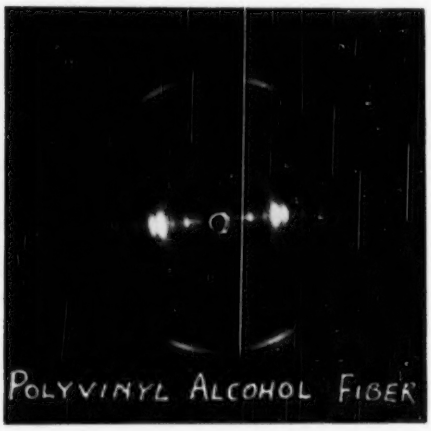


FIG. 1. *X-ray diffraction patterns.*

Under annealing conditions a reflection corresponding to the second lateral direction can be detected in the x-ray diagram. Because of the presence of an asymmetric carbon atom in each unit of a vinyl polymer, there must be a high degree of disorder along the chain. The amount of disorder which can be accommodated in a crystal lattice depends upon the relative sizes of the substituent groups. Thus, hydroxyl can be exchanged for hydrogen, as in the polyvinyl alcohol lattice, without appreciable distortion. The chlorine in polyvinylchloride produces a more defective lattice, and the nitrile in polyacrylonitrile is just large enough to cause disruption of the crystal lattice. The phenyl group in polystyrene exceeds the size which can be fitted into a lattice at random, and this polymer is entirely amorphous.

While the nature of the x-ray diffraction diagrams does not permit much more to be learned about the structure of this polymer, the above facts are in good agreement with many other observed properties and with the evidence of structure obtained by infrared spectroscopy. From the standpoint of solubility, the observed low degree of order in two directions is probably fortunate, since such a high-melting polymer should prove even more difficult to dissolve.

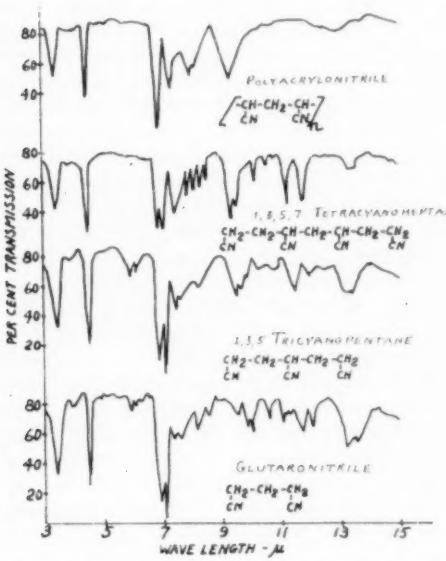


FIG. 2. *Infrared absorption spectra of polyacrylonitrile and low-molecular-weight analogs.*

Some information has been obtained on the structure of polyacrylonitrile by means of infrared absorption spectra obtained on transparent films of the polymer. In order to assist in the interpretation of the resulting curves, certain structural analogs have been synthesized and their spectra compared with the spectra of the polymer. The curves are shown in Figure 2.

At 3.3 μ, the C—H stretching band is common in all of the species, and indicates similarity. Likewise, at 4.4 μ the C≡N stretching band is common. At 7.0 μ the strong C—H stretching doublet in the analogs becomes single in the polymer, probably because the C—H effects in a multiplicity of —CHCN and —CH_2— groups are averaged out. Above this frequency, the individual bands in the monomeric analogs are complex, probably because there are numerous structural effects, and have not been individually assigned. This would require careful analysis of numerous structural analogs. However, it is to be expected that these specific vibration frequencies in the monomers would become averaged out in a long polymer chain, resulting in the smoother curve (top) observed for polyacrylonitrile. The unidentified doublet at 9.3–9.5 μ in glutaronitrile (bottom) deepens, becomes less complex (single), and shifts slightly to the left, going through the more complex analogs to the polymer. The bands at 13.2–13.6 μ could be CH_2 twisting, analogous to propane. The 8.0 μ band may be —CHCN bending. At any rate, these are other complicated regions which become more simplified in the polymer. While more infrared data would be desirable to establish this point, indications are that by far the major proportion of the polymer is a product of the simple 1,2 head-to-tail addition which has been postulated.

There are some indications of the existence of minor amounts of other linkages in the polymer. One is that it is frequently somewhat yellowish in color, whereas the normal head-to-tail linkages theoretically cannot produce strong absorption in the visible region of the spectrum. Another is that the nitrogen content of the polymer is usually somewhat below the theoretical 26.4%. Kern and Fernow [8] attempted to account for the low nitrogen content by the splitting out of HCN during polymerization, and they reported actually finding some HCN. In analyzing polyacrylonitrile, it has been found necessary to dry the polymer very carefully, since it absorbs 1.5% to 2% moisture very rapidly from laboratory

air of moderate humidities, in spite of its low degree of total water absorption when soaked. Kern and Fernow may not have recognized this, and this may account, at least partially, for their low nitrogen values. In the work herein reported, small amounts of HCN were found, but the quantities detected have not been adequate to account for the low nitrogen content by a dehydrocyanation reaction.

Kern and Fernow also considered the possibility that other types of linkages exist in the polymer because of the fact that on saponification only about 95% of the nitrogen could be recovered as ammonia. Experiments in our laboratory have demonstrated that the nitrogen found in the polymer by Kjeldahl or Dumas analyses can all be recovered as ammonia by long boiling with 30% aqueous sodium hydroxide solution. Thus, it does not appear that there is any unsaponifiable nitrile or other type of nitrogen. However, this evidence is not sufficient to rule out the possibility that a small amount of nitrogen is linked in some other way than as normal side-chain nitriles.

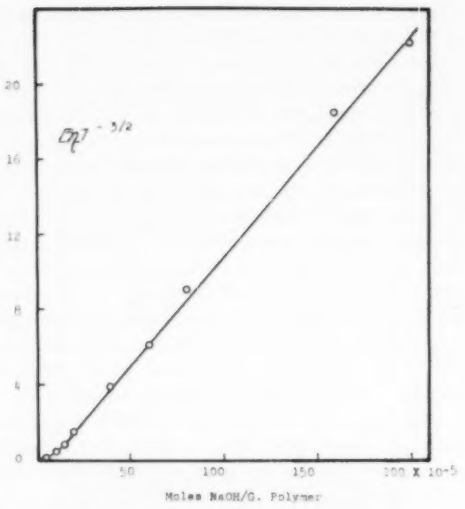


FIG. 3. *The stoichiometric relationship for the alkaline degradation of polyacrylonitrile.*

Color Formation in Polyacrylonitrile

Orlon acrylic fiber can now be manufactured which is white in color. Under certain conditions, however, polyacrylonitrile becomes yellowish or brown during polymerization, in its solutions, or in the dry state. Color formation has yielded some interesting information about the polymers. Discoloration in solution is accelerated by heating and by the presence of oxygen from the air. In an inert atmosphere, such as nitrogen, color formation proceeds more slowly. The molecular weight of the polymer also drops on heating in solution, while polyacrylonitrile yarns are unusually stable to molecular-weight degradation on heating. At room temperature in solution with dimethylformamide little or no molecular-weight degradation occurs. However, the addition of dilute aqueous alkali to these solutions causes an almost instantaneous decrease in molecular weight [13]. For example, 10^{-3} moles of sodium hydroxide added to 5 g. of the polymer in dimethylformamide decreased the intrinsic viscosity from 3.3 to 1.5 and the corresponding number-average molecular weight from 110,000 to 19,000. Experiments in which the base was added and then quickly neutralized indicated that the reaction was complete in a very short time, probably not requiring more than 1 sec. Little further change in viscosity occurred when the material was allowed to stand an appreciable length of time after this initial reaction. A stoichiometric relationship was found to exist between the number of chain cleavages and the quantity of sodium hydroxide added. Results are shown in Figure 3. From the existence of this relationship, together with certain theoretical derivations by Montroll and Simha [14], it can be concluded that a random chain-scission reaction has taken place. It has been calculated from the molecular weight of these polymers that approximately 1 to 2 molecules of sodium hydroxide are required for the scission of one link in the polymer. In experiments of this kind, as many as 300 bonds per polymer molecule have been broken. Since this number is far greater than the possible number of abnormal links which the infrared data suggest might be present, it seems that normal lengths in the head-to-tail polymer structure have been broken.

Further evidence of the nature of the degradation has been provided by the high recoveries of the degraded polymer from the reaction mixture. These were all about 90%, with no trend toward smaller percentage recoveries for higher alkali concentrations; this is about the amount of polymer recovered in the control samples to which no alkali had been added.

The addition of alkali is accompanied by the im-

mediate appearance of an orange color. Upon acidification, this color changes to a light yellow.

Of a number of mechanisms which have been proposed to account for these phenomena, none is entirely satisfactory. Judging from the characteristics of the reaction, a study of the end-groups resulting from cleavage should yield pertinent information as to the nature of the reaction. This might be done by direct chemical methods or by infrared investigations.

Orlon acrylic fiber has good stability under conditions of high-temperature treatment. It can be ironed repeatedly and effectively without discoloration. Under more drastic heating treatments, its physical properties hold up remarkedly well, but color changes do occur, going progressively to yellow, brown, and black as heating is continued. The data in Table IV illustrate the surprisingly good physical properties of yarn which has been heated until it is jet black. Similar yarns had good properties even after heating for 60 hours at 200°C. They were insoluble in several good polyacrylonitrile solvents, had somewhat greater water absorption, and had also increased in breaking temperature (measured under 0.5 g.-per-den. load) to 250°C, as compared to 172°C for the control. Fibers thus treated contained basic groups, as indicated by the absorption of mineral acids. The tensile properties would obviously not have been retained if there had been any extensive polymer-chain degradation. Dry acrylonitrile polymers evidently do not undergo random chain-scission reactions such as that observed for alkali-treated solutions.

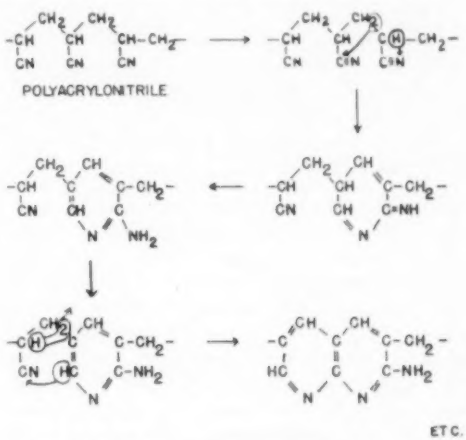
The black yarn is remarkably stable to further heating, even in a Bunsen burner flame. Very little combustion takes place, the samples of yarn or fabric merely glowing in the flame. Samples so treated lost only about 30% of their total initial weight before the original heat treatment. Such yarns or fabrics still have a fair amount of strength and flexibility, although they are brittle by textile standards.

TABLE IV. POLYACRYLONITRILE YARN PROPERTIES AFTER HEATING

Treatment	Dry tenacity (g./den.)	Wet tenacity (g./den.)	Dry elongation (%)	Wet elongation (%)
200°C, 16 hrs., air	1.94	1.77	9.3	9.2
200°C, 16 hrs., nitrogen	2.87	2.78	12.9	13.7
Control, not heated	3.42	3.35	15.7	17.0

Flamed samples have been analyzed for carbon, hydrogen, and nitrogen content. The values for these components add to only 85%–90%, which may mean that oxygen was introduced or that combustion to end-products was incomplete. Materials with such high flame-stability are known to be difficult to analyze by combustion methods. This point is being further investigated.

There is as yet no exact chemical evidence as to the nature of the reaction which takes place during these treatments. These products must still be essentially linear polymeric in form in order to retain fiber properties. Any chemical structures postulated must be of a type known to be extremely stable thermally. Also to be taken into account are the facts that the heated materials have increased in water-sensitivity and are basic. A condensed aromatic-ring system, analogous to the heterocyclic compounds formed during the destructive distillation of coal, would account for these known properties as well as for the intense color. Such a reaction might occur as follows:



This reaction would involve dehydrogenation, as is indicated by the analyses. As pointed out above, the analysis can be interpreted to indicate some oxidation, so that the condensed pyridine type of ring formation is probably not the only reaction which has occurred, at least in the flaming step. The theoretical hydrogen content of this condensed ring structure is 2.0%. The actual hydrogen content has

dropped from 5.7% in the control (theoretical for polyacryonitrile) to 2.3%.

Attempts have been made to obtain some information about the structure of the heated and flamed samples by means of infrared absorption measurements. However, the absorption bands were so wide and deep as to defy interpretation.

Fiber Properties

Reports on many of the properties of Orlon acrylic fiber which were discussed in the complete version of this paper presented at New London have already been published [10, 15], and these properties will therefore be treated here only in summary.

Orlon acrylic fiber generally has a dumbbell- or dog-bone-shaped cross section. The core is of somewhat lower density than that of the skin, resulting in a fiber density of 1.12–1.17. This low density indicates good covering power in fabrics. Orlon has approximately the same tenacity, elongation, elastic recovery, and stretch-resistance as natural silk, and in hand and luster it is also remarkably silk-like. It has very low water absorption and also low moisture regain.

In Figure 4 are shown a number of stress-strain curves for various yarns. The similarity of Orlon acrylic fiber to silk in stress-strain behavior is at once apparent. Of the two samples of Orlon which appear on this graph, the variety which will be produced in the May Plant (at Camden, S. C.) is the silk-like one. By variations of processing conditions

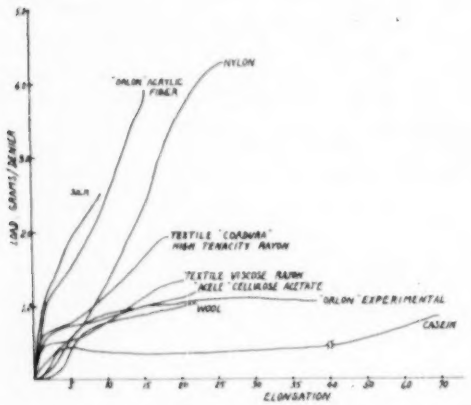


FIG. 4. *Stress-strain curves for various yarns. Constant rate of elongation: 10% per min.*

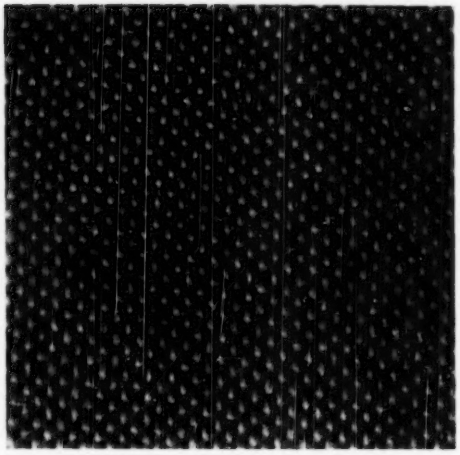


FIG. 5. *Sample illustrating resistance of polyacrylonitrile to sulfuric acid. Fabric prepared in 1942 for initial market evaluations. Sample immersed in 25% sulfuric acid for 7 days at 75°C. No measurable change in fiber properties resulted.*

it is possible to produce a wide range of properties. The curve for the sample marked "'Orlon' Experimental," which is also under development, shows that it approximates wool rather closely in stress-strain behavior. It has also been found to exhibit wool-like behavior in fabrics. Both types of Orlon have good bulking power, and in thermal insulation tests have been shown to be as warm as, or actually warmer than, wool.

Probably the outstanding characteristic of Orlon is its resistance to weathering factors, especially sunlight, corrosive atmospheres, and biological attack by insects or by microorganisms. It has marked resistance to degradation by heat and by a wide variety of acidic chemicals. Its resistance to alkalies is considerably less, but entirely adequate for purposes of laundering.

The resistance of polyacrylonitrile fibers to mineral acids is surprising, considering the fact that monomeric nitriles react rather readily to form amides and ammonium salts. Resistance to sulfuric acid by woven fabrics which were submitted for trade-testing in 1942 is illustrated in Figure 5. Fiber properties of the treated sample were not significantly different from those of the untreated sample. Results of many other tests of chemical resistance are reported elsewhere [10].

Because of the remarkable dimensional stability and freedom from shrinkage in laundering of Orlon acrylic fiber, and owing to the fact that it takes up very little moisture when wet, fabrics have shown remarkable durability in laundering. Shirts made from Orlon have been laundered 60–70 times over a 2-year period without perceptible change in dimensions or signs of wear. If articles of apparel are laundered without being sharply creased while hot, they usually require no ironing. Where required, the fabrics iron very easily either dry or slightly damp, using the "rayon" setting on home irons. When blended with wool, Orlon acrylic staple has shown remarkable ability to stabilize the blend against shrinkage. An Orlon content of as little as 15% in a blend with wool has stabilized wool socks against shrinkage under standard laundering conditions. Its abrasion-resistance, determined by a number of methods, is inferior to that of nylon by a considerable margin, but has been consistently better than that of a number of cellulosic fiber samples.

Dyeing

The variety of Orlon acrylic fiber which is being made in limited quantities at present at Waynesboro, and which will be produced in the May Plant, cannot be said to have general commercial dyeability. Another type of Orlon is being made experimentally, which has vastly improved dyeing properties.

Under special conditions the Orlon produced at the present time can be dyed to good shades with dispersed (acetate) dyes and with certain vat dyes. It also accepts pastel shades of azoic and basic dyes. Acid dyes stain it very lightly or not at all. Basic dyes can be applied in shades of moderate depth, but show characteristic poor light-fastness. Acetate and vat dyeings are discussed below in greater detail.

With the acetate dyes, pastel shades are obtained at the boil or below. Under pressure—for example, by using a pad-pressure-steam technique—heavy shades can be obtained. At 10–15 p.s.i. for 15 min., two to three times as much dye is taken up as at the boil. A very few examples of the many dyes which can be applied by using this method are Acetamine Yellow CG, Acetamine Orange GR, and Celanthrene Pure Blue BRS.

A method of obtaining good dyeings at the boil was found in the use of "carriers." These are phenolic compounds, such as *m*-cresol, which have limited solubility in the dye bath, but penetrate the fiber readily. *m*-Cresol must be used in about 2% concentration (based on dye-bath volume) for this purpose. "Carriers" evidently penetrate the fiber by a solution process. The amount absorbed is proportional to the dye-bath concentration. That *m*-cresol prefers the fiber to the bath is indicated by the fact that the partition coefficient is considerably greater than 1. Because of the volatility of *m*-cresol from boiling dye baths, it must be used with good ventilation. The quantity required makes it rather uneconomical. It can, however, be efficiently removed from the fiber by normal boil-off procedures; tests on fabrics so treated have shown no dermatitis hazards.

Acetate dyes on Orlon in general show light-fastness slightly superior to that for the same dyeings on acetate yarns. Wet-fastness is excellent. Exhaust is rather poor (30%–40%) but can be improved somewhat by addition of *m*-cresol to the bath to act as a "carrier."

The thioindigoid type of vat dyes can be applied to Orlon under certain conditions. Anthraquinone types have not been successfully applied. The former can be applied at the boil, at relatively high pH's (9.5–12), to give excellent light-fastness and good wash-fastness but poor crock-fastness, owing to poor penetration of the fibers. At pH's of 7.5–10, *m*-cresol assists the dyeing markedly. The use of potassium carbonate in relatively large amounts also greatly improves depth of shade, in contrast to other alkali-metal carbonates. Oxidation of the leuco requires relatively drastic conditions—for example, 1–3% nitric acid and 30 min. at the boil.

Vat dyeings have been markedly improved in depth of color and in fiber penetration (resulting in good crock-fastness) by the use of pressures of, say, 15 lbs. for 30 min. These have given exhausts of the order of 70%. Although shades were dull, wash- and light-fastness were excellent. The pad-pressure-steam process has also been used, with results approaching those of dye baths under pressure. The fibers are damaged by more drastic alkaline treatment.

The experimental basified Orlon dyes far better than does the present product. A wide range of acid dyes having excellent wash- and crock-fastness and fair to excellent light-fastness can be applied at the boil. However, relatively strong acid dye baths (pH 2–3) are required. This presents a problem in dyeing of mixed viscose-Orlon fabrics. In wool-Orlon blends, the much higher rate of dyeing of the wool is a problem in the application of acid colors.

Many acetate-type colors can also be applied at the boil. These show the usual good wet-fastness and moderate light-fastness.

Dyeing the experimental basified Orlon with vat colors is more satisfactory than that of the present product. A number of good deep shades can be applied at the boil. These have light-fastness as good as, or better than, that of the same dyes on cotton.

The problems which have been encountered in the dyeing of Orlon are the result of its "hydrophobic" nature, because of which the rates of diffusion into the fiber are very slow. However, the results obtained to date indicate that practical solutions to these problems are possible.

Summary

Orlon acrylic fibers are made from polymers containing large percentages of acrylonitrile. Their production has been made possible by the discovery of a number of unreactive organic solvents for such polymers. The solvents, which are of several chemical classes, are characterized by polar molecular groupings which apparently bond with and solvate the polymer molecules. The applicability of current theories of polymer solubility is discussed.

Polyacrylonitrile has been separated by precipitation methods into fractions which indicate normal molecular-weight distribution. A relationship between intrinsic viscosity and molecular weight is given. The polymer chains have a high degree of order in only one lateral direction. The structure appears to be almost completely that of a normal head-to-tail vinyl addition polymer.

Polyacrylonitrile fibers have remarkable resistance to heat, but gradually darken during heat treatments. A theory of the chemical changes involved is discussed. The contrasting behavior of polyacrylonitrile in solution, in which a stochiometric random chain-scission reaction occurs in the presence of alkali, is described.

Brief discussions of physical properties and of dyeing characteristics of two types of Orlon acrylic fiber are presented.

Acknowledgment

Contributions to the research on which this paper is based have been received from many members of the du Pont research staff, to whom grateful acknowledgment is made. In addition to the literature references, special assistance by the author's colleagues Drs. C. E. Black and D. L. Green on the topics on x-ray, infrared, and heat treatments, and by Dr. C. S. Marvel on various phases of the work is acknowledged.

Literature Cited

1. Astle, M. J., and McConnel, W. V., Polarographic Investigations of Hydrogen Bonding: I: *ortho*- and *para*-Nitrophenols, *J. Am. Chem. Soc.* **65**, 35-8 (1943).
2. Coltof, W., Establishment and Application of Rules for the Interaction Between High-Molecular Solutes and Organic Solvents, *J. Oil & Colour Chemists' Assoc.* **23**, 176-209 (1940).
3. Copley, M. J., Zellhoefer, G. F., and Marvel, C. S., Hydrogen Bonds Involving the C—H Link, *J. Am. Chem. Soc.* **60**, 2666-73 (1938); **62**, 227-8 (1940).
4. Flory, P. J., Thermodynamics of High Polymer Solutions, *J. Chem. Phys.* **9**, 660-1 (1941).
5. Flory, P. J., Thermodynamics of Dilute Solutions of High Polymers, *J. Chem. Phys.* **13**, 453-65 (1945).
6. Flory, P. J., and Leutner, F. S., Occurrence of Head-to-Head Arrangements of Structural Units in Polyvinyl Alcohol, *J. Polymer Sci.* **3**, 880-90 (1948).
7. Huggins, M. L., Thermodynamic Properties of Solutions of Long-Chain Compounds, *Ann. N. Y. Acad. Sci.* **43**, 1-32 (1942).
8. Kern, W., and Fernow, H., Macromolecular Compounds; CCCII: Polymerization of Acrylonitrile: Polyacrylonitrile, *J. prakt. Chem.* **160**, 281-95 (1942); *Rubber Chem. and Technol.* **17**, 356-65 (1944).
9. Lanzl, G. F., E. I. du Pont de Nemours and Co., to be published in more detail in a separate publication.
10. Larsen, W. E., Scheiderbauer, R. A., and Wilfong, R. E., "Orlon" Acrylic Fiber, *Sci. Monthly* **69**, No. 6, 414-18 (1949).
11. Marvel, C. S., Copley, M. J., and Ginsberg, E., Hydrogen Bonds Involving the C—H Link, *J. Am. Chem. Soc.* **62**, 3109-12 (1940).
12. Marvel, C. S., and Inskeep, G. E., End Group Structure of Polyvinyl Alcohol, *J. Am. Chem. Soc.* **65**, 1710-14 (1943); and earlier papers in this series.
13. McCartney, J. R., E. I. du Pont de Nemours and Co., to be published in more detail in a separate publication.
14. Montroll, E. W., and Simha, R., Theory of Depolymerization of Long Chain Molecules, *J. Chem. Phys.* **8**, 721-7 (1940).
15. Quig, J. B., "Orlon" Acrylic Fiber—A New Synthetic, *Papers of AATT* **4**, 61-70 (Mar. 1949).
16. Rein, H., Survey of Synthetic Fiber Developments, *Angew. Chem.* **60**, 159-61 (1948).

17. Rein, H., Bei Polyacrylonitril-Faser, *Angew. Chem.* **61**, 241–5 (1949).
18. Rein, H., Die synthetischen Fasern: Ein Überblick über ihre bisherige und künftige Entwicklung, *Melliand Textilber.* **30**, 243–6 (1949).
19. Rein, H., Die synthetischen Fasern: Ein Überblick über ihre bisherige und künftige Entwicklung, *Melliand Textilber.* **30**, 299–301 (1949).
20. Schultz, C. V., Determination of Molecular Weights of Series of Polymers of High Molecular Weight Substances by Osmotic Measurements, *Z. physik. Chem.* **A176**, 317–37 (1937).
21. Spurlin, H. M., Polymer Solutions, *J. Polymer Sci.* **3**, 714–34 (1948).

Patents

(The patents listed in items 22–36 (all dated July 23, 1946) deal with solutions of polyacrylonitrile in organic solvents.)

22. Houtz, R. C., U. S. Pat. 2,404,711.
23. Houtz, R. C., U. S. Pat. 2,404,713.
24. Latham, G. H., U. S. Pat. 2,404,714.
25. Rogers, A. O., U. S. Pat. 2,404,715.
26. Hansley, V. L., U. S. Pat. 2,404,716.
27. Houtz, R. C., U. S. Pat. 2,404,717.
28. Houtz, R. C., U. S. Pat. 2,404,718.
29. Houtz, R. C., U. S. Pat. 2,404,720.
30. Houtz, R. C., U. S. Pat. 2,404,721.
31. Houtz, R. C., U. S. Pat. 2,404,722.
32. Merner, R. R., U. S. Pat. 2,404,723.
33. Houtz, R. C., U. S. Pat. 2,404,724.
34. Rogers, A. O., U. S. Pat. 2,404,725.
35. Charch, W. H., U. S. Pat. 2,404,726.
36. Houtz, R. C., U. S. Pat. 2,404,727.
37. Rein, H., U. S. Pat. 2,117,210, Manufacture of Shaped Articles of Polymeric Acrylic Acid Nitrile (May 10, 1938).
38. Rein, H., U. S. Pat. 2,140,921, Manufacture of Solutions of a Polymerized Vinyl Compound (Dec. 20, 1938).

(*Manuscript received May 1, 1950.*)

A Mechanized Fiber Blender

Lyle E. Hessler and Herbert E. Kieke

Cotton Research, Texas Technological College, Lubbock, Texas*

THE DIFFICULTIES of properly sampling raw cotton are apparent to many fiber technologists. Variations in fiber properties have been demonstrated over the fiber, seed, lock, plant, field, and growing season. These variations, together with damage to fiber caused by weathering, which can be very irregular, make the blending and sampling of cotton for physical testing very important. As increased instrument testing for fiber properties becomes more and more common in the textile industry, fiber sampling, fluffing, and blending can no longer be ignored where instrument accuracy is required. The axiom, "accuracy of physical testing can be only as good as sampling," is still a very good criterion to follow in any fiber analysis.

Many laboratories sample cotton by hand, which is extremely tiresome and time-consuming. Moreover, manipulation by hand introduces the human element, which may vary with each sample and each operator. For uniform sampling, a mechanical method is usually the best, providing it does not overwork the fiber. Blenders and analyzers can injure the fiber, and before they are adopted they should therefore be tested to ascertain the amount of damage which they may do to the fiber. Recently, Kreible [1] demonstrated by degree-of-polymerization studies that considerable damage occurs in the mechanical processing of cotton; hence care must be taken not to overwork the fiber prior to testing.

A hand blender described by Stewart [2] and later mechanized (Figure 1) at Texas Technological College for greater ease of operation is discussed here in detail.

Description of Blender

The mechanization of the rolls, as shown in Figure 2, can be done in a number of ways, but the rolls must be made according to exact specifications for the greatest efficiency of operation in cleaning and randomizing. The two rolls, which are 14 in. long and 3½ in. in diameter, are covered with regular card-stripper wire so that the angles of the wire will be down and toward each other as the wires mesh. When one roll revolves toward the other, such an arrangement allows the moving roll to hook the fiber and remove it from the stationary roll with the least amount of interference. In blending cotton, for the best operation the depth of mesh is roughly to the "knee," or about ¾ in.

The mechanization of the rolls may be readily accomplished in any machine shop with materials on hand. With the rolls operating at only 100 to 150 r.p.m., the hardwood support for the rolls can serve as bearings. A ¼ H.P. ratio motor is a suitable source of power. The pin clutch shown in Section A-A of Figure 1 is simple and trouble-free when operated at the speed suggested above. By moving the clutch lever to the left, the clutch pin may be made to enter the hole on the 51-tooth gear, turning it counterclockwise and thus powering the train of gears which turns the back roll. When the clutch lever is shifted to the right, the clutch pin engages the hole in the disc which is fastened to the shaft that drives the front roll clockwise. Such a mecha-

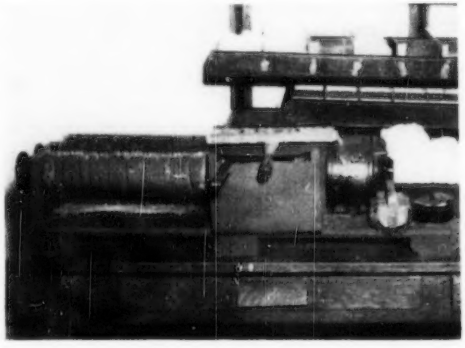


FIG. 1. *Photograph of fiber blender.*

* One of the laboratories sponsored by The Cotton Research Committee of Texas.

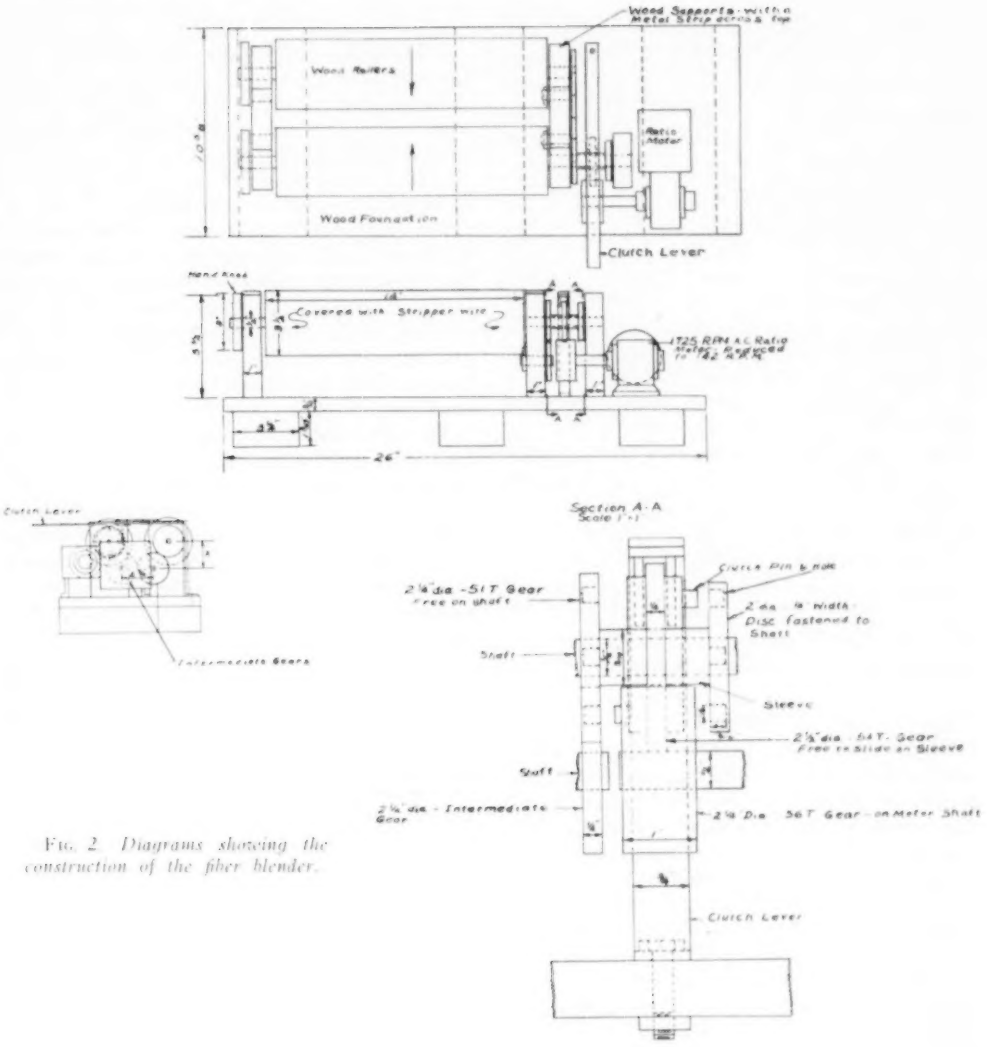


FIG. 2. *Diagrams showing the construction of the fiber blender.*

nism gives independent action to the two rolls used in randomizing the fiber.

Operation of Blender

For randomizing cotton, about 3 to 4 g. of fiber is evenly distributed in a thin layer over the back roll. The blender is then ready for mixing the cotton from roll to roll. The operator shifts the lever to the left, driving the back roll at full speed for several seconds. This action parallelizes the fibers and removes foreign matter by brushing the cotton against the slower-turning front roll. A shift of the lever to the right sets in motion the front roll, and with a light tension on the hand wheel of the back roll the cotton is transferred from the back to the front roll for fur-

TABLE I. STRENGTH AND STANDARD DEVIATION IN SAMPLING COTTON FIBER BY FIVE DIFFERENT METHODS

Sample No.	Method of sampling	No. of breaks	Strength in 1,000 lbs./ sq. in.	Standard deviation
1	Fiber blender	500	82.7	1.56
2	Shirley Analyzer	500	82.0	2.43
3	Ribbon lapper	500	81.7	1.86
4	Picker lap	500	81.1	1.67
5	Hand sampled	500	80.9	2.38
	Average	500	81.7	1.98

ther randomizing. This operation is repeated a number of times, depending on the condition of the cotton to be blended and sampled. After a thorough randomizing and cleaning, the cotton is ready for doffing. This is done by shifting the lever to a neutral position, and, with the cotton on the back roll, a brush made of stripper wire is used to slowly peel the cotton from the roll. The turning of the roll backward, in removing the cotton, is facilitated by the small hand wheel on the blender, shown at the left in Figure 1. The doffing operation, if properly executed, will give a well-blended, fluffy mass from which samples may be taken as desired.

Results

When cotton has been randomized, only after a large number of tests can the uniformity of a given quantity be established. Therefore, cotton of unknown character must be thoroughly blended in order for a sample to be representative of the whole.

Available at Texas Technological College for the past 3 years has been a highly uniform bale of check cotton on which thousands of different physical tests have been made; and because this lot is so very uniform, blending and sampling studies made on it are considered to be of value. Pressley strength and standard deviation were determined in 500 individual tests on five different samples from the check bale: one hand-blended; one blend from the Shirley Analyzer; one blend of fibers from processing equipment for spinning (opening equipment, picker, card, and ribbon lapper); one blend from opening equipment (through the picker); and one blend from the fiber blender under discussion. The results are given in Table I.

Discussion

Little fiber or waste is removed when the hand-sampling method is used. Strong fibers are more apt to be removed than weak ones. Therefore, the low strength value and one of the highest standard deviations, listed for this method, in Table I are easily explained on the basis that the sample was run "as is," with all the weaker fibers present.

The Shirley Analyzer removes all the trash and some of the weak and short fibers. At high rates of speed the Shirley Analyzer also has a tendency to cut and damage some of the longer, weaker fibers. The high standard deviation which occurs in this type of sampling is difficult to explain, except to say that perhaps it does better cleaning than sampling of cotton fiber.

The samples from the two spinning processes were low in strength because of the mechanical working the fiber received. The sample from the ribbon lapper was also carded, which accounts for its greater strength over that from the picker lap, since the card takes out much short, weak fiber. These two samples had low standard deviations, possibly due to the removal of approximately 5 to 10% of the poorer fibers and waste.

The sample from the fiber blender under consideration yielded samples with the highest strength and the lowest standard deviation. Furthermore, Fibrograph determinations showed conclusively that there was no change in fiber length after a long period of randomization. The high strength and no change in length, which indicate that the cotton has not been injured, and the low standard deviation in strength tests are evidence of the advantages of the fiber-blender method over the other four methods for blending, randomizing, and sampling cotton fiber.

Acknowledgment

The authors wish to acknowledge assistance in statistical work by Mr. Joel F. Hembree, Cotton Merchandising Research, University of Texas, Austin, Texas.

Literature Cited

1. Kreible, J. G., and Whitwell, J. C., TEXTILE RESEARCH JOURNAL **19**, 556 (1949).
2. Stewart, Ruby E., TEXTILE RESEARCH JOURNAL **15**, 468 (1945).

(Manuscript received July 17, 1950.)

Trace Metals in Cotton Fiber

D. C. Heinzelman and R. T. O'Connor

Southern Regional Research Laboratory, New Orleans, Louisiana*

INVESTIGATIONS of the trace-metal content of cotton and cotton products have been concerned in the past only with plant nutrition [2] or with the presence in cotton fiber of those trace metals which are known to accelerate the deterioration of rubber [4, 5]. The spectrochemical investigations described here were undertaken in order to determine the amounts of trace metals naturally present in cotton fibers, so as to provide basic data for anticipated problems concerned with trace metals in cotton and cotton products.

Two groups of fiber samples were obtained from the 1948 experimental productions through the cooperation of the Bureau of Plant Industry, Soils, and Agricultural Engineering. One consisted of fibers of 8 varieties (Table I) grown at Stoneville, Mississippi, and the other of fiber of the Coker 100 Wilt variety grown at each of 13 locations (Table I) representing the environments of the cotton-production areas. To assure that the samples as analyzed represented the cotton fiber as produced by the plant, the cotton bolls were picked just before opening and allowed to dry, care being taken to prevent contamination with field-blown dust, and the fiber was removed by hand without the use of any metal instrument or apparatus. The spectrograms were examined quantitatively for copper, iron, and manganese, and qualitatively for aluminum, boron, chromium, nickel, tin, and zinc.

Spectrochemical Analysis

The spectrochemical analysis, based on the line-width method of Coheur [3], was carried out as described previously [7], with the usual precautions being observed. Some special features of the techniques employed are reported in the following paragraphs.

In preparing the working curves, in order to avoid any diverse ion effect [1], a matrix was used which approximated the ash of cotton fiber with respect to the presence of major constituents and which was free from traces of the metals to be determined. It consisted of 65.18% potassium carbonate, 0.96% sodium chloride, 11.02% calcium carbonate, 18.70% magnesium carbonate, and 4.14% germanium dioxide. Germanium, which is not present in the ash of cotton fiber, was included to function as an internal standard. Graded amounts of solutions of the ele-

TABLE I. Ash Content and Spectrochemical Analysis of Specified Cotton Fiber for Copper, Iron, and Manganese (Moisture-Free Basis)

Variety and location	Ash (%)	Copper	Iron	Manganese
		Parts per million		
Stoneville, Miss.				
Acala 4-42	1.42	1.99	11.55	7.22
Acala 1517	1.41	1.60	12.19	7.21
Rowden 41B	1.28	1.74	10.84	5.36
Mebane (Watson)	1.36	1.01	5.91	3.18
Stoneville 2B	1.19	1.53	12.55	6.28
Deltapine 15	1.09	1.40	7.90	5.90
Coker 100 Wilt	1.13	1.59	11.14	7.46
Wilds	1.26	1.00	7.97	4.91
Average	1.27	1.48	10.01	5.94
Coker 100 Wilt				
Statesville, N. C.	1.53	1.55	6.88	7.44
Florence, S. C.	1.26	2.10	7.29	9.08
Tifton, Ga.	1.26	1.67	7.91	9.30
Auburn, Ala.	1.56	0.78	9.03	8.90
Jackson, Tenn.	1.22	1.45	7.25	9.20
Stoneville, Miss.	1.13	1.59	11.14	7.46
St. Joseph, La.	1.33	0.68	3.74	2.79
Chickasha, Okla.	1.37	1.13	7.25	7.87
Greenville, Tex.	1.22	1.95	7.03	8.42
College Station, Tex.	1.26	4.01	13.77	8.17
State College, N. M.	1.56	1.05	4.85	5.82
Sacaton, Ariz.	1.49	2.72	12.89	12.39
Shafter, Calif.	1.35	0.93	5.60	5.81
Average	1.37	1.66	8.05	7.90
All samples				
Highest	1.56	4.01	13.77	12.39
Lowest	1.09	0.68	3.74	2.79
Average	1.32	1.57	9.03	6.92

* One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

ments being determined were added to portions of the matrix in Vycor dishes to provide standards. The standards were dried *in vacuo* over phosphorus pentoxide and subsequently heated on a hot plate at approximately 300°C to remove the last traces of moisture. The mass was then transferred to a mortar, using a silver spatula, and thoroughly ground and mixed, during which time heating was necessary because of the hygroscopic nature of the mixture.

Five-gram samples of the cotton fiber were ashed in triplicate in tared Vycor dishes covered with inverted Pyrex funnels [6]. The samples were charred on a hot plate for 1 to 2 hrs. and then ashed overnight at 450°C in a muffle furnace the temperature of which had been raised in increments of about 25°. The samples were removed from the furnace and cooled, so that traces of the ash could be brushed from the funnel, and crushed. They were then returned to the furnace and the ashing was continued for 3 hrs. at 450°C in an attempt to remove residual carbon. After cooling in a desiccator, the dishes were weighed for the determination of the ash contents of the original samples; these contents ranged from 1.09% to 1.56% on a moisture-free basis (Table I). Volumes of an aqueous solution of germanium dioxide (2.1594 g. per liter) which were proportional to the average ash contents, respectively, of the particular samples were added to the ashes so as to introduce into each the 4.14% of the oxide which was characteristic of the matrix, to serve as the internal standard. The ashes were then dried, ground, and mixed as described for the standards.

The spectra of the standards and samples were photographed on Eastman S. A. No. 1 plates * using a Littrow-type spectrograph set to cover the region from 2,500 to 3,450 Å. and with a rotating sector set to permit only 18.8% of the light to enter the slit of the instrument. Portions of the ash weighing 5 mg. each were weighed into the craters of highly purified carbon electrodes, and the arcing was accomplished under the influence of a 225-volt, 20-ampere direct current for 90 sec. in order to assure complete consumption of the sample.

The widths of the selected lines of each spectrogram were measured from profiles obtained by use of an automatic recording microphotometer. The spectral lines which were selected for analysis were those at 3,269.49 Å. for germanium, 3,273.96 Å. for copper, 3,020.64 Å. for iron, and 2,576.10 Å. and 2,949.20 Å. for manganese.

All qualitative tests, except those for boron and zinc, were made on the plates prepared for the quantitative analyses. The spectra of boron and zinc, the sensitive lines of which appear at wave lengths less than 2,500 Å., were photographed on Eastman No. 103A-O plates at the instrument setting of 2,100 Å. to 2,500 Å. without the use of a rotating sector.

Results

The results of the spectrochemical analysis of the twenty samples of selected cotton fiber for copper, iron, and manganese are given in Table I. The over-all precision is ± 20% deviation from the mean and, except in rare cases, it is well within ± 15%. Recovery tests on known amounts of the elements added to samples already analyzed and complete analyses of known standards (Table II) showed that the over-all accuracy of the method is also within the same range.

TABLE II. RECOVERY TESTS AND ANALYSIS OF KNOWN SAMPLES

Sample	Amount originally present	Total amount present*	Amount recovered	Deviation (%)
	Parts per million			
Cotton and added metal				
Cu	0.96	2.96	2.87	− 3.0
Cu	1.44	3.44	2.52	−26.7
Cu	0.99	2.99	2.75	− 8.0
Fe	5.60	9.60	9.30	− 3.1
Fe	7.47	11.47	12.52	+ 9.2
Fe	6.87	10.87	13.73	+26.3
Mn	6.82	10.82	13.03	+20.4
Mn	3.02	7.02	7.91	+12.7
Mn	8.55	12.55	12.61	+ 0.5
Synthetic ash				
Cu	40		42.7	+ 6.8
Cu	100		85.1	−14.9
Cu	200		214	+ 7.0
Fe	400		468	+17.0
Fe	1,000		977	− 2.3
Fe	1,600		1,860	+16.3
Mn	210		214	+ 1.9
Mn	841		871	+ 3.6
Mn	2,000		1,740	−13.0

* In the recovery tests 2 parts per million of Cu, 4 of Fe, and 4 of Mn were added to each sample.

* The mention of trade products does not imply that they are endorsed by the Department of Agriculture over similar products not mentioned.

The analytical results show marked differences between the trace-metal contents of the samples of cotton fiber; these are attributed to variety and soil environment, the latter including the trace-metal elements in the fertilizers used. The lowest values for copper, iron, and manganese are all for the sample of Coker 100 Wilt from St. Joseph, Louisiana, whereas the highest values are for the samples of the same variety from College Station, Texas, and Sacaton, Arizona. The ranges in the trace-metal contents of the lint of a single variety grown on different soils at the selected locations are considerably greater than those of the lints of 8 varieties grown on a single soil at one location. The precision and accuracy tests described above indicate that the differences attributed to variety and environment are real.

The spectrograms revealed no traces of chromium, nickel, or tin in any of the samples, in spite of the fact that these metals are frequently reported to be present in cotton lint and cotton textiles. This leads to the assumption that if present, they are the result of accidental contamination during processing or manufacture. Aluminum, boron, and zinc appeared to be present in small quantities in all cases.

Summary

The lint of 8 varieties of cotton grown in one location and of one variety grown in 13 locations was analyzed for trace metals by the line-width method of spectrochemical analysis to provide compositional data on the presence of metals which are known to catalyze the degradation of cotton cellulose. Modifications were made in the line-width method of spectrochemical analysis as previously applied to vegetable oils to make it more applicable to cotton fiber. The highest, the lowest, and the average values, calculated on a moisture-free basis, for copper, iron, and manganese were 4.01, 0.68, and 1.57; 13.77, 3.74, and 9.03; and 12.39, 2.79, and 6.92 parts per million, respectively. Although some of the variation is attributed to varietal characteristics, the greater part is attributed to soil environment.

The spectrograms showed the presence of aluminum, boron, and zinc in trace amounts in all cases, but they did not reveal the presence of chromium, nickel, or tin.

Acknowledgment

The assistance of the Bureau of Plant Industry, Soils, and Agricultural Engineering, through H. D. Barker, in providing the seed-cotton samples is gratefully acknowledged.

Literature Cited

1. Brode, W. R., "Chemical Spectroscopy," 2nd Ed., New York, John Wiley & Sons, 1943.
2. Chilean Nitrate Educational Bureau, Inc., "Bibliography of the Literature on the Minor Elements and Their Relation to Plant and Animal Nutrition," 4th Ed., New York, Chilean Nitrate Educational Bureau, 1948.
3. Coheur, P., *J. Opt. Soc. Am.* **36**, 498 (1946).
4. Dufraisse, C., "Autoxidation and Deterioration by Oxygen, Prooxygens, and Antioxygens," in Chap. XIII in "Chemistry and Technology of Rubber," edited by C. C. Davis and J. T. Blake, New York, Reinhold Publishing Corp., 1937.
5. Holst, W. A., Jr., *Dyestuffs* **37**, 138–45 (1942).
6. O'Connor, R. T., Heinzelman, D. C., and Jefferson, M. E., *J. Am. Oil Chem. Soc.* **24**, 185–9 (1947).
7. O'Connor, R. T., Heinzelman, D. C., and Jefferson, M. E., *J. Am. Oil Chem. Soc.* **25**, 408–14 (1948).

(*Manuscript received July 17, 1950.*)

Book Reviews

Mothproofing. R. W. Moncrieff. London, Leonard Hill Ltd., and New York, Mapleton House, 1950. 200 pages. Price, $3.75.

(Reviewed by H. Luttringhaus, General Dyestuff Corporation, New York)

This book represents the first attempt which has been made to treat the entire subject of mothproofing.

The book's 17 chapters cover all aspects of mothproofing. The chapters on the different types of clothes moths and carpet beetles are competent, but would have been more complete if reference had been made to papers published by E. Titschack on clothes moths and by R. Slabaugh on *Attagenus piceus*.

In the chapter on the damage to wool caused by pests, mention is made that chlorination does not make wool immune to attack by moths. It might have been of theoretical interest to mention that overchlorination of wool and also long exposure to light impart a certain moth-repellency (according to *American Dyestuff Reporter*, Jan. 26, 1948, p. 58).

The history of mothproofing with dyestuffs which finally resulted in the production of colorless products like Eulan CN and Mitin FF is given and many fluorides are well described.

The Eulans are treated extensively. For the American reader it is a little confusing to find only the European names, like "Eulan CNA" or "Eulan CN Extra." The American woolen industry knows this product under the name "Eulan CN," and the American reader might get the mistaken impression that there really is something "extra" about the European product. Eulan CNA is a weaker agent, and it would be correct to use 2%–3% of this product; however, Eulan CN Extra is not recommended to be applied in amounts of 2%–3%, but 1½%–2%.

As for Eulan CN, this reviewer would like to point out that this type was sold in the U. S. before it was available on the European market. The American reader who is acquainted with Eulan CN will question the statement that it has to be applied with acid, especially if he should be a manufacturer who has been using Eulan CN from a neutral bath for years.

All the statements on fastness properties are rather vague, and instead of expressing an open opinion based on his own tests the author quotes from patents or the literature of the manufacturers; hence the reader will be greatly at a loss if he depends on the material in this section to familiarize himself with the qualities of mothproofing agents.

There seems to be a question in the author's mind as to whether an acid dyestuff can be called fast to washing. Products like the milling types in general are usually fast enough to washing, and since the fastness to washing of products like Eulan CN and Mitin FF is comparable to that of milling-type products, acid dyestuffs and mothproofing agents can be called fast to washing if they survive the service life of the garment.

Mitin FF is discussed thoroughly as to development, constitution, and application. The different brands of Mystox are likewise comprehensively discussed.

The various methods of applying DDT are described and discussed, together with the disadvantages of the product. It should have been mentioned that DDT migrates onto untreated material with which it comes in contact, and investigators should therefore be cautioned that washed samples which have been in contact with the original treated ones show good resistance at times. The same holds true for many fluorides.

The chapter on Eulan NK (Eulan NKF) and other phosphonium compounds gives the principles of application. The main field of application should have been mentioned—namely, the treatment of mixtures of white and dyed wool at 100°F in the washer.

The chapter on the nutritional requirements and the digestion of the clothes-moth larvae is very good. While the book has many good illustrations, the collection would have been more complete if pictures pertaining to digestion of wool by the larvae, published by Textile Research Institute, Inc., New York, in "Mothproofing of Woolen Materials in Europe," had been reproduced, or at least mentioned.

The author devotes more space to the modification of wool than to any other subject. The Glyoxal

Process is written of in an optimistic way that is "catching" to the reader.

Mothproofing during dry-cleaning, precautions against damage, and breeding of moths are handled adequately.

The account of testing of mothproofed samples is written very well. However, the author seems to be a bit too uncritical when it comes to the standardization of test methods. Unfortunately, testing of mothproofed materials is not as simple as the author would like to believe.

The refinement becomes a necessity when a near-quantitative evaluation of a mothproofing agent has to be made. There are borderline cases which have to be taken into consideration, and then the decision should be based only on a good standardized method which has been generally accepted. That is the reason why in the U.S. much time is spent on improving the present tentative methods.

In spite of the foregoing criticisms, this book is a successful attempt to compile for the first time many data on mothproofing in such a way as to make good, informative reading for everyone interested in mothproofing.

Handbuch der Färberei und anderer Prozesse der Textilveredlung. Vols. III and IV. Albert Schaeffer. (In German.) Stuttgart, Konradin-Verlag Robert Kohlhammer, 1950. Vol. III, 361 + vii pages; Vol. IV, 246 + viii pages. Price, $9.17.

(Reviewed by L. Fusser, General Dyestuff Corporation, New York)

Volumes I and II were reviewed in the February, 1950, issue of TEXTILE RESEARCH JOURNAL, page 136.

The third volume, the experimental part of the "Handbuch der Färberei," contains two sections. In the first, the experimental application of all classes of dyestuffs to textile fibers is given in detail. By means of many precisely outlined experiments, the effect of the various factors which enter into the dyeing processes is clearly demonstrated. For instance, tests are presented which show the leveling action of sulfuric acid in the application of metallized acid dyes; the improvement in wet-fastness of some direct dyes when aftertreated with complex copper compounds; the light sensitivity of the leuco esters of vat dyes before development; and many other effects which are most instructive to the student.

As a laboratory guide in the application of dyestuffs to textiles, this part of the book can be highly recommended. One criticism is the meager treatment given the dyeing of silk and nylon, and the absence of any discussion of the experimental dyeing of the newer synthetic fibers.

The second part of the third volume deals with fastness tests. A critical discussion precedes the presentation of the testing methods and procedures for evaluating test results as established by fastness committees in various countries. Justifiably, the author points out the lack of uniformity in methods and in rating of test results. Although some beginnings towards international conformity have been made, progress in this respect can be expected to be slow; witness the fact that in the third edition of the *Color Index*, now in preparation, ratings will be given as obtained by American, British, and Continental European test methods. It is, unfortunately, a fact that even results arrived at by using the methods of the AATCC are not infrequently rated differently in the pattern cards and literature of the dyestuff manufacturers in the U. S. All of the official and tentative test methods of the American, British, and German fastness committees are presented side by side. The Swiss and Russian methods were not included, because they were either incomplete or unavailable at the time the book went to press. Nevertheless, anyone concerned with the fastness properties of colored textiles will find Dr. Schaeffer's treatment of the subject highly useful as well as interesting.

The fourth and final volume comprises the analytical section. It covers the identification and quantitative separation of the fibers, the identification of dyestuffs in substance and on the fiber, the determination of inorganic and organic compounds on the fiber, and hydrogen ion concentration and pH control in textile processing. An endeavor was made to present only those analytical methods which had proved to be practical and which can be readily carried out in a mill laboratory.

For the identification of undyed fibers, various dye-stain mixtures are suggested, with colored charts to illustrate the results obtainable. The stains, the usual chemical reactions, and the microscopical appearance of the fiber are arranged in convenient tabular form

—however, photographs of fiber cross sections are not presented. The quantitative separation of fibers is dealt with fully.

In the chapter on identification of dyestuffs, the determination of the class of dyestuffs which may be present on a textile has been stressed, since this is usually what the dyer or mill chemist needs to know. For those who wish to pursue this difficult subject further, directions are given which are very helpful in the identification of individual dyes.

The determination of inorganic and organic compounds on the fiber is based on microanalytical methods. Reagents are employed which are sufficiently sensitive for the small quantities of chemicals involved when small samples of textiles are being analyzed, yet not so sensitive as to indicate the presence of mere trace elements.

The significance of the pH value and the electrometric and colorimetric methods for its determination are thoroughly discussed, together with applications of its measurement in the wet-processing of textiles.

Both volumes contain extensive bibliographies, are well indexed, and are well printed on a good grade of paper.

After perusing the four volumes of this "Handbook" one is impressed with the scope and thoroughness with which the task has been carried out. Anyone who studied these four volumes and had the opportunity to perform the experiments outlined therein would certainly acquire the equivalent of a college or textile-school course in textile chemistry and dyeing.

Clark's Weave Room Calculations. W. A. Graham Clark. Third Edition. Charlotte, North Carolina, Clark Publishing Co., 1949. 244 pages. Price, $5.00.

(Reviewed by Gerald B. Fletcher, Georgia Institute of Technology, Atlanta, Ga.)

This third edition of "Clark's Weave Room Calculations", is, in the reviewer's opinion, particularly valuable for the manufacturer. By the term "manufacturer" is meant the "man in the mill." It is an excellent handbook with a thorough coverage of calculations. The formulas are simplified and full explanation is made as to their derivation: each is illustrated by one or more examples.

The section entitled "Typical American Cotton Cloths" provides a valuable store of information on yarn numbers and constructions of standard cotton fabrics. It should prove a valuable reference book for sales offices as well as for mill men.

TEXTILE RESEARCH INSTITUTE, INC.

LABORATORIES AND GENERAL OFFICES

KINGSTON-PRINCETON ROAD, PRINCETON, N. J.

PUBLICATIONS DEPARTMENT

10 EAST 40TH STREET, NEW YORK 16, N. Y.

OFFICERS

A. G. Ashcroft, *President*
Kenneth Wilson, *Vice-President*
Richard T. Kropf, *Treasurer*
P. C. Alford, Jr., *Secretary*

BOARD OF DIRECTORS

Term Expires 1952	*Term Expires 1951*	*Term Expires 1950*
Norman C. Armitage	F. Eugene Ackerman	A. G. Ashcroft
Andre Blumenthal	Joseph H. Brant	Robert Burns
Ephraim Freedman	Miles A. Dahlen	W. J. Fullerton
Thomas G. Hawley, Jr.	Bertrand W. Hayward	J. B. Goldberg
G. P. Hoff	Richard T. Kropf	Henry Herrmann
Jules Labarthe, Jr.	H. Wickliffe Rose	C. H. Masland, II
Donald H. Powers	Leonard Smith	Edward T. Pickard
W. Bailey Sellars	Kenneth Wilson	H. Gordon Smith

EXECUTIVE COMMITTEE

Andre Blumenthal, *Chairman*

A. G. Ashcroft	Richard T. Kropf	H. Gordon Smith
J. B. Goldberg	H. Wickliffe Rose	Kenneth Wilson

DIRECTOR OF RESEARCH

John H. Dillon

DEPARTMENT HEADS

James H. Wakelin, *Associate Director of Research*
P. C. Alford, Jr., *Administrative Assistant to Director of Research*
K. Lanse Turner, *Assistant to Director of Research, Field Engineer*

Julian S. Jacobs, *Director of Publications*
10 East 40th Street
New York 16, New York

Edward T. Pickard, *Advisor on Economic Research and Education*
Kent, Connecticut

RESEARCH ADVISORY COMMITTEE

Miles A. Dahlen, *Chairman*	Warren E. Emley	G. K. Lake
William D. Appel	J. B. Goldberg	Donald H. Powers
A. G. Ashcroft	M. E. Heard	Walter M. Scott
F. Bonnet	G. P. Hoff	Hugh S. Taylor
Joseph H. Brant	H. Y. Jennings	Werner von Bergen
Malcolm E. Campbell	Richard T. Kropf	Albert C. Walker